

October, 1933

RUBBER CHEMISTRY AND TECHNOLOGY

Published under the Auspices of the
RUBBER DIVISION of the AMERICAN CHEMICAL SOCIETY



VOLUME VI

NUMBER 4



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RUBBER CHEMISTRY AND TECHNOLOGY

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Editor.....C. C. DAVIS
Advertising Manager.....E. R. BRIDGWATER
Secretary-Treasurer.....H. E. SIMMONS

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October, 1933

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues (\$2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

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All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers, and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

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Rubber Division Activities

The Rubber Division of the American Chemical Society

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Sergeant-at-Arms.....	C. W. CHRISTENSEN

The Fall Meeting of the Rubber Division of the American Chemical Society in Chicago, Illinois, September 11, 12, and 14, 1933

The fall meeting of the Rubber Division was held in the Stevens Hotel, Chicago, with three hundred present.

First Session

Symposium on the Progress of Chemistry in the Rubber Industry

1. H. L. Fisher and R. H. Gerke. A review of the structure of the rubber hydrocarbon.
2. Ira Williams. The mechanism of vulcanization.
3. N. A. Shepard, J. N. Street and C. R. Park. Fillers and reinforcing agents.
4. R. A. Crawford. Organic age-resisters in rubber compounds.

Second and Third Sessions

5. Melvin Mooney. A shearing plastometer for unvulcanized rubber.
6. C. E. Barnett. Thermal properties of rubber compounds. I—Thermal conductivity of rubber and rubber-compounding materials.
7. J. H. Doering. Some service tests on tires and tubes in which the rubber was exclusively guayule.
8. A. A. Somerville and W. F. Russell. The effect of temperature on the tensile properties of vulcanized rubber.
9. R. E. Morris. Temperature coefficient of vulcanization.
10. E. W. Booth and R. L. Shipley. A Comparison of oxygen-bomb, Geer oven and air-bomb aging tests.
11. Thomas Midgley, Jr., Albert Henne, and Alvin F. Shepard. Natural and synthetic rubber. XII. Reversible vulcanization by organometallic derivatives.
12. A. R. Kemp. Further studies on the iodine value of rubber and gutta hydrocarbon as determined by iodine chloride.
13. V. N. Morris. Fluorescence of rubber and of compounding ingredients.
14. B. A. Jones. An automatic, modified falling sphere viscometer.
15. H. F. Palmer. The testing of reclaimed rubber.
16. J. H. Dillon. Rubber plasticity control.

Fourth Session

17. W. K. Lewis, Lombard Squires, and Robert Nussbaum, Jr. The mechanism of the vulcanization of rubber with sulfur.

18. Robert Nussbaum, Jr., Lombard Squires, and C. C. Smith. The effect of cure on the physical properties of a high sulfur-rubber mix.

19. W. K. Lewis, Lombard Squires, and A. J. Sysko. The effect of oxygen on the plasticization of rubber.

20. C. K. Novotney. Thinning and gelation of rubber cements.

21. H. R. Thies and A. M. Clifford. Plioform. A new thermoplastic molding material.

22. W. F. Busse and J. M. Davies. The development of structures in uncured rubber on standing.

The BANQUET was held in the Bal Tabarin, Hotel Sherman, on the evening of September 12 with two hundred sixty-two in attendance. Souvenirs for the dinner were donated by the following companies:

American Zinc Oxide Co.
Binney & Smith Co.
Chemical & Pigment Co.
E. I. du Pont de Nemours & Co.
J. M. Huber, Inc.
Midwest Rubber Reclaiming Co.
New Jersey Zinc Co.
Rubber Service Laboratories Co.
United Carbon Co.
Wishnick-Tumpeer, Inc.

Anaconda Zinc Oxide Co.
Godfrey L. Cabot, Inc.
Dryden Rubber Company
General Atlas Carbon Co.
Inland Rubber Co.
Naugatuck Chemical Co.
Philadelphia Rubber Works Co.
Henry L. Scott Co.
R. T. Vanderbilt Co.

The following officers were elected for the coming year: *Chairman*, Ira Williams; *Vice-Chairman*, S. M. Cadwell; *Secretary-Treasurer*, H. E. Simmons; *Executive Committee*, L. B. Sebrell, F. W. Stavely, J. T. Blake, H. J. Conroy, Carl Frick; *Sergeant-at-Arms*, C. W. Christensen.

Minutes of the Outgoing Executive Committee

Meeting on September 12, 1933, with the following present: L. B. Sebrell, E. R. Bridgwater, Ira Williams, E. B. Curtis, L. C. Peterson, A. F. Pond, C. W. Christensen, F. W. Stavely, H. E. Simmons. C. C. Davis, Editor of RUBBER CHEMISTRY AND TECHNOLOGY, also met with the Committee.

E. R. Bridgwater was elected Advertising Manager of RUBBER CHEMISTRY AND TECHNOLOGY. After some discussion relative to further advertising, L. B. Sebrell was instructed to look after the securing of a subsidy from the Rubber Manufacturer's Association for the next two issues of RUBBER CHEMISTRY AND TECHNOLOGY.

The Treasurer discussed the frozen funds of the Rubber Division in the Standard Bank of Akron (this amount is \$2436.05), and presented the reorganization plan prepared by this bank requiring the depositors to subscribe for stock in the new bank to the extent of 50 per cent of the frozen deposits. This will enable the bank to open its doors and free one-half of our deposit.

The Committee instructed the Chairman and Treasurer to subscribe for stock in the reorganization plan to the extent of one-half of our restricted account. The Treasurer was also instructed to dispose of this stock as soon as possible after opening of the bank.

H. E. SIMMONS, *Secretary-Treasurer*

Minutes of the Newly Elected Executive Committee

The meeting was held on September 14, 1933, with the following present: Ira Williams, *Chairman*, H. E. Simmons, E. B. Sebrell, J. T. Blake, H. J. Conroy, Carl Frick, C. E. Christensen.

It was agreed that the papers comprising the Symposium on the Progress of Chemistry in the Rubber Industry should not be published at the present time, but become the basis of a Monograph; additional papers to be prepared for the Spring Meeting and then all to be edited in this form. The responsibility of working this out was placed in the hands of the Chairman, Ira Williams.

The Secretary made the following report, which by motion was accepted and ordered a part of the minutes.

Secretary's Report

Total membership to date.....	406
Regular members.....	293
Associate members.....	89
New members.....	24
Members not paid for 1933.....	54
Associate members not paid for 1933.....	20
New members for 1932—did not renew membership.....	5
Subscriptions paid for 1933.....	85
Old subscriptions renewed.....	63
New subscribers.....	22
Subscriptions not renewed for 1933.....	21
New subscriptions for 1932 not renewed 1933..	4
Honorary members and exchanges.....	32

Treasurer's Report

Money in restricted account.....	\$2436.05
Money received from dues, subscriptions, advertising and from the Rubber Manufacturers' Ass'n.....	\$2820.31
Expenditures:	
Mack Printing Company.....	\$1496.47
Office supplies and printing.....	72.10
Translations.....	376.48
Expenses of Secretary to Washington....	75.00
Stenographic service.....	60.00
Tax on checks, exchange on foreign check and collections due to bank moratorium	5.54
	2085.59
Balance in the bank September 9, 1933.....	\$734.72
Money in restricted account.....	\$2436.05
Money in bank Sept. 9.....	734.72
Money due from advertisers in July issue...	480.28
Total.....	\$3651.05

The question of the spring meeting in St. Petersburg, Florida, was considered, and it was voted that the meeting be held in St. Petersburg unless in the mind of the Chairman conditions are such that it would be impracticable to hold the meeting in that city.

H. E. SIMMONS, *Secretary-Treasurer*

[The following circular letter to scientific journals has been received from the International Office of Chemistry at Paris, and is published in RUBBER CHEMISTRY AND TECHNOLOGY for the benefit of those interested.]

The International Organization of Chemical Documentation

Questions concerning documentation have of late assumed more and more importance. Scientific and technical documents increase on all sides in such numbers that it becomes more and more difficult to gather useful material for the benefit of enquirers. There are many bodies that deal permanently with the registering, classing, and diffusion of such documents. Now the coördination of the respective activities of these institutions on an international basis has become necessary in order to permit them to carry on their work efficiently.

As regards the province of chemistry, a step was taken in 1932 in the scientific and technical sphere by the entry into activity of the International Office of Chemistry, created by international convention, and having its headquarters in Paris.

Its first act was the summoning of a Conference of Experts, which included the following personalities: Messrs. F. Donker Duyvis, Member of the Council of Patents, The Hague; P. Dutoit, Professor at the University of Lausanne; F. Haber, Director of the Kaiser-Wilhelm Institut für Physikalische Chemie und Electrochemie, Berlin; E. Hauser, Member of the Academy of Sciences, Madrid; Ch. Marie, Secretary General of the Comité International des Tables Annuelles de Constantes, Paris; N. Parravano, Member of the Academy of Italy, President of the Comitato Nazionale di Chimica, Rome; G. Peny, President of the Federation of Chemical Industries of Belgium, at Brussels; J. C. Philip, professor at the Imperial College of Science and Technology, London.

The work of this Conference of experts led to the adoption of a certain number of recommendations fixing the three principal tasks of the Office:

I—To render accessible to all interested persons the already existing documentation, accumulated in the various centers, depots, and collections.

II—To guide the chemical documentation which is in course of production in such a way as to facilitate its registering, filing, and diffusion, by methods found to be the best.

III—To assure coördination between the documentation relative to chemistry and that concerning other scientific knowledge in the field of international documentation.

Thanks to these varied operations, the users of such documentation will find that all over the world a practical and rational organization of documentation in chemistry is being carried out systematically and progressively, liable to be more and more effectively adapted to their needs.

New Books and Other Publications

Rubber in Chemical Engineering. By Henry P. Stevens and M. B. Donald. Issued by the Rubber Growers' Association, Inc., London, England. Paper cover booklet. 55 pp.

This book describes the present position of rubber as applied to the chemical and allied industries and should be of help to engineers in general and chemical engineers in particular in gaining a better knowledge of the field in which rubber has already been applied. The book is fully illustrated and indexed and contains chapters devoted to the properties and chemical resistance of rubber, rubber linings for tanks and the like, rubber paints, cements, etc., and the chemical uses of rubber. [From the *Rubber Age* of New York.]

"Rubber and Automobiles." By Colin Macbeth. With foreword by F. W. Lanchester. Issued by The Rubber Growers' Association, Inc., 2, 3, and 4 Idol Lane, Eastcheap, London, E. C. 3, England. May, 1933. Paper, 109 pages, 5½ by 8¾ inches. Charts, Index.

This book is intended primarily for all those interested in the manufacture, supply, and use of rubber for automobiles. It contains the following separate sections bound together in a loose-leaf cover to facilitate the inclusion of additional matter: tire development, rubber in suspension systems, rubber chassis parts attached to frame, rubber in power plant, rubber in transmission systems, rubber in braking systems, rubber in steering systems, rubber in coachwork, body constructions and seatings, rubber in electrical systems, rubber latex, rubber specifications and standards.

Rubber as a major item in the suspension system is a novelty to the average motorist. The book, however, shows a number of directions in which this use of rubber is being developed. It is only necessary to consider rubber usage in tires and their vastly increased efficiency to realize the benefits likely to accrue to the motorist when satisfactory ways of using rubber on the suspension systems have been proved and adopted. [From the *India Rubber World*.]

Annual Report 1932. Published by the Rubber Research Institute of Malaya, August, 1933. Paper cover booklet. 148 pp. Price \$1.00.

The contents of this booklet, including a number of tables, are as follows: Annual Report of the Board; Annual Accounts for the year 1932; Annual Report of the Director; Annual Report of the Soils Division; Annual Report of the Botanical Division; Annual Report of the Pathological Division; Annual Report of the Chemical Division; Annual Report of the Rubber Roadways Investigations; Annual Report of the Librarian; Annual Report of the Experiment Station; Annual Report of the Field Division; Annual Report of the London Advisory Committee for Rubber Research (Ceylon and Malaya). [From *The Rubber Age* of New York.]

The History and Description of Clones of Hevea Brasiliensis. By C. E. T. Mann and C. C. T. Sharp. Illustrated by H. C. Chuan. Published by the Rubber Research Institute of Malaya. August, 1933. Planting Manual No. 5. Price \$2.00.

The scope of this manual is to present in concise form the more important characters together with records of yield performance of the various Clones of *Hevea brasiliensis* that have been established and used in commercial plantings during recent years. [From *The Rubber Age*, of New York.]

"Bulletin of the National Research Council." August, 1933, No. 91. Industrial Research Laboratories of the United States Including Consulting

Research Laboratories. Fifth Edition Compiled by Clarence J. West and Callie Hull for the Research Information Service. National Research Council, United States. Published by The National Research Council of The National Academy of Sciences, Washington, D. C., 1933. Paper, 223 pages, 6³/₄ by 9³/₄ inches. Indexed by geographical distribution and subject classification. Price \$2.

The industrial research laboratories of the United States to the number of 1575 are listed in this edition with information regarding their personnel and lines of work. Laboratories connected with federal, state, or municipal governments or with educational institutions have been excluded from this survey. [From the *India Rubber World*.]

"1933 A. S. T. M. Manual on Presentation of Data with Table of Squares and Square Roots." Sponsored by Committee E-1 on Methods of Testing. Published by the American Society for Testing Materials, Philadelphia, Pa. Paper, 45 pages, 6 by 9 inches. Price 50¢.

This manual was prepared by a special committee of engineers, who are statistical experts, to make available in convenient form some of the principles of efficient presentation of data. The manual discusses the application of statistical methods to the problems of (1) condensing information contained in a set of observations and (2) presenting the essential information in a concise form more readily interpretable than the unorganized mass of original data. Attention is directed particularly to quantitative information on measurable characteristics of materials and manufactured products.

Besides pointing out important measures or values especially useful for summarizing information contained in a set of observations, the committee has given methods of computation, etc.

In a particular instance the functions of the data which should be presented depend upon what uses are to be made of them; accordingly a section is devoted to essential information.

The manual also gives critical comments on various methods used in presenting data, a discussion of what relevant information should accompany the data, and the committee's recommendations for data presentation. [From the *India Rubber World*.]

Sulfuric Acid as a Latex Coagulant

J. L. Wiltshire

KUALA LUMPUR, FEDERATED MALAY STATES

The replacement of formic or acetic acid by sulfuric acid for coagulating has the obvious attraction of saving money, but this acid undoubtedly has a bad reputation among planters, and the published literature on the subject is not encouraging. Several authors of standard books on estate practice have emphasized the results of Martin,¹ who observed that the addition of one-eighth of one per cent of sulfuric acid to dry rubber caused a very marked retarding effect on the rate of vulcanization. As, however, the total amount of acid used for coagulation is approximately one-half of one per cent, and by far the greatest proportion of this will be removed in the serum and in the wash-water, it seems unlikely that any quantity approaching Martin's figure would be allowed to remain in the rubber. Martin's results can be regarded as nothing more than a warning, and certainly do not constitute any real evidence of the unsuitability of sulfuric acid.

Eaton² studied the subject more exhaustively, and found that rubber coagulated with sulfuric acid did, in general, show a lower rate of vulcanization than acetic acid rubber. The greatest differences were found in slab rubber, and the effect on sheet and crepe was very much smaller. In some of the figures reported for sheet there was practically no difference at all. Eaton lays particular stress on the fact that any such effects are greatly magnified by the use of an excess of acid over the minimum. This fact, coupled with the very large retardation shown by slab, is a strong indication that any effects of sulfuric are not caused by direct chemical action during coagulation but by the delayed action of that part of the acid which is retained by the rubber.

De Vries³ also records the retarding effect of this acid, but states quite definitely that "when the minimum quantity is used the difference between the rubber coagulated with it and with acetic acid is small and such small quantities can be used without objection." He also reports that the aging properties of rubber coagulated with a minimum quantity of sulfuric acid are perfectly satisfactory. No special deterioration could be detected unless large quantities were used—such as one part of acid to 22 parts of rubber. The normal proportion is approximately one part to 160 parts of rubber.

Morgan⁴ in his standard text-book is distinctly conservative but states that sulfuric acid may be used *in the very smallest quantity* without harmful results. He recommends that it should only be used in the absence of the commoner and much safer coagulants.

The unpopularity of the acid among planters is probably due to some extent to the published statements noted above, but undoubtedly its chief cause is a very lively—even exaggerated—realization of its corrosive properties. This can be remedied by experience, and several well-known estates have been using sulfuric acid for many years with almost complete freedom from accidents.

The information previously available may therefore be summarized thus:

- (1) Sulfuric acid is perfectly satisfactory as regards the actual coagulation.
- (2) It is harmful to the rubber if used in excessive quantities.
- (3) It is particularly harmful under certain conditions which lead to the retention of a large proportion of the acid in the rubber.

(4) If used in minimum quantities and removed as completely as possible, the harmful effects are negligible.

(5) It has been shown by experience that the corrosive properties do not constitute any bar to the efficient use of sulfuric acid, provided it is used with intelligent caution.

The published figures for the amount of acid required, together with the market quotations for formic and sulfuric acids, showed that the introduction of the latter would halve the cost of the coagulant, *i. e.*, by reducing it from 0.10 to 0.05 cent per pound. It was therefore decided to carry out certain confirmatory experiments with a view to collecting sufficient evidence to enable considered advice to be given on this subject.

Experiments on the Quantity of Coagulant

A series of coagulations were carried out with varying quantities of sulfuric acid and the resulting coagula were machined at the appropriate time. The acid was introduced about noon, and any coagulum not sufficiently firm for machining by 4 P. M. was allowed to remain until 8 A. M. the following morning. The time of machining is therefore described as "same day" or "next day." The method of machining was the same throughout, and each coagulum was passed through six machines with definite clearances. In every case one gallon of latex of D. R. C. 1½ was coagulated. The area of each dried sheet was determined by measurement, and since each sheet is of the same weight and has had the same mechanical treatment, this area may be regarded as a very fair indication of the "softness" of the coagulum at the time of machining.

For convenience in the laboratory, all quantities of acid are expressed in terms of grams of pure acid of specific gravity 1.84. These figures may be converted to more practical units using the equivalent: 2.0 grams of pure acid per pound of dry rubber is equal to one fluid ounce of pure acid per 26 pounds of dry rubber.

The results of these experiments are shown in the table.

TABLE I

Sheet No.	Quantity of Latex	D. R. C.	Quantity of Acid, G. per Lb.	When Machined	Area of Dry Sheet
1	1 gallon	1½ lb. per gal.	1.33	Next day	534 sq. in.
2	1 gallon	1½ lb. per gal.	1.33	Next day	549 sq. in.
3	1 gallon	1½ lb. per gal.	2.00	Same day	579 sq. in.
4	1 gallon	1½ lb. per gal.	2.00	Same day	570 sq. in.
5	1 gallon	1½ lb. per gal.	2.00	Next day	405 sq. in.
6	1 gallon	1½ lb. per gal.	2.00	Next day	375 sq. in.
7	1 gallon	1½ lb. per gal.	2.66	Same day	{ Sheet spoiled in machining
8	1 gallon	1½ lb. per gal.	2.66	Same day	
9	1 gallon	1½ lb. per gal.	2.66	Next day	512 sq. in.
10	1 gallon	1½ lb. per gal.	2.66	Next day	480 sq. in.

The coagulation in samples Nos. 1 and 2 was not very satisfactory—the serum being slightly cloudy and the coagulum rather uneven. With 2.0 grams per pound Nos. 3 and 4 machined on the same day without any difficulty, but with 2.66 grams per pound the coagulum was too soft for same-day machining. This is a most important point, and in any factory experiments with sulfuric acid it must be remembered that reducing the quantity of acid may give a faster coagulation. It must also be emphasized that if the acid used is the quantity sufficient for same-day machining and the coagulum is allowed to remain till next day, it will then be unnecessarily hard. This is shown by the area figures recorded for the various sheets.

Thus samples 3 and 4 have spread to an area of approximately 570 sq. in. but the same coagulum left till next morning gives a sheet of approximate area 390 sq. in.—a reduction of 32 per cent. This, of course, represents a corresponding increase in thickness and in time of drying. The experiments recorded below will furnish very potent reasons for maintaining the thickness of sulfuric acid sheet at a minimum.

In view of these remarks it will be seen that for normal practice of machining "next morning," the most suitable quantity of acid is about 2.7 grams of pure acid per pound of dry rubber. Figures have been obtained from certain estates for the quantity actually in use, which agree with these laboratory results. Thus one estate coagulating at $1\frac{1}{4}$ lb. per gallon used $3\frac{1}{2}$ fluid ounces of acid per 50 gallons of latex, *i. e.*, 2.9 grams per pound. Another estate coagulating at 1 lb. per gallon uses 1 oz. of acid per 20 pounds, *i. e.*, 2.6 grams per pound of rubber.

Vulcanizing Properties of Sulfuric Acid-Coagulated Rubber

The vulcanization of the various samples has been carried out under the standard conditions previously described in THIS JOURNAL by Bishop and Fullerton. All tensile properties are expressed as a modulus—the stress in kilograms per square mm. for an elongation of 650 per cent. From each sample three mixes are cured, and six rings are pulled corresponding to each time of cure. If more than three of these six rings fail to reach 650 per cent elongation the sample is regarded as over-cured.

The samples vulcanized correspond to Nos. 3 and 9 in Table I, *i. e.*, at 2.0 grams per pound machined the same day and 2.7 grams per pound machined the next day. For comparison, two acetic acid-coagulated sheets were also treated—one from same-day machining and one from next-day machining.

TABLE II

Sample No.	Acid	Grams per Pound	Machined	Modulus Kg. per Sq. Mm. at 650 Per Cent				
				Elongation Time of Cure, Minutes				
				80	100	120	130	140
3	Sulfuric	2.0	Same day	0.48	0.79	1.16	1.31	Over-cured
9	Sulfuric	2.7	Next day	0.38	0.64	0.92	..	1.25
11	Acetic	4.1	Same day	0.46	0.72	1.05	1.21	Over-cured
12	Acetic	2.8	Next day	0.67	1.15	1.39	Over-cured	(110)

These results are better expressed in graphical form, and reference to Fig. 1 will show immediately the small retarding effect of sulfuric acid.

In sheet coagulated with acetic acid, the effect of same-day machining is to retard the rate of cure, whereas with sulfuric acid the sheet machined on the same day is faster curing than that machined the following day. In both cases these differences may be attributed to the fact that coagulum machined only a few hours after the addition of the acid is machined thinner and is washed more efficiently than the tougher coagulum obtained by overnight coagulation. The controlling factor in acetic acid sheet is the amount of serum constituent remaining, and the actual acid—being volatile—is of little importance. Hence a well washed rubber is slower curing, as shown by the difference between sheet and crepe. In sulfuric acid sheet the retarding effect of the acid is of greater importance than the accelerating effect of the serum components. Hence the well-washed sheet is faster curing. All these sheets have been air-dried, and it is the general rule that air-dried are somewhat slower curing than smoked sheets.

The retarding influence is, however, not very great, and extreme difference between the times for reaching the maximum modulus is only 30 minutes, *i. e.*, between 110

and 140 minutes. The maximum moduli attained by the sulfuric acid sheets are also of the same order as those given by the acetic acid sheets. The experiments support the statements made above that the use of sulfuric acid in minimum quan-

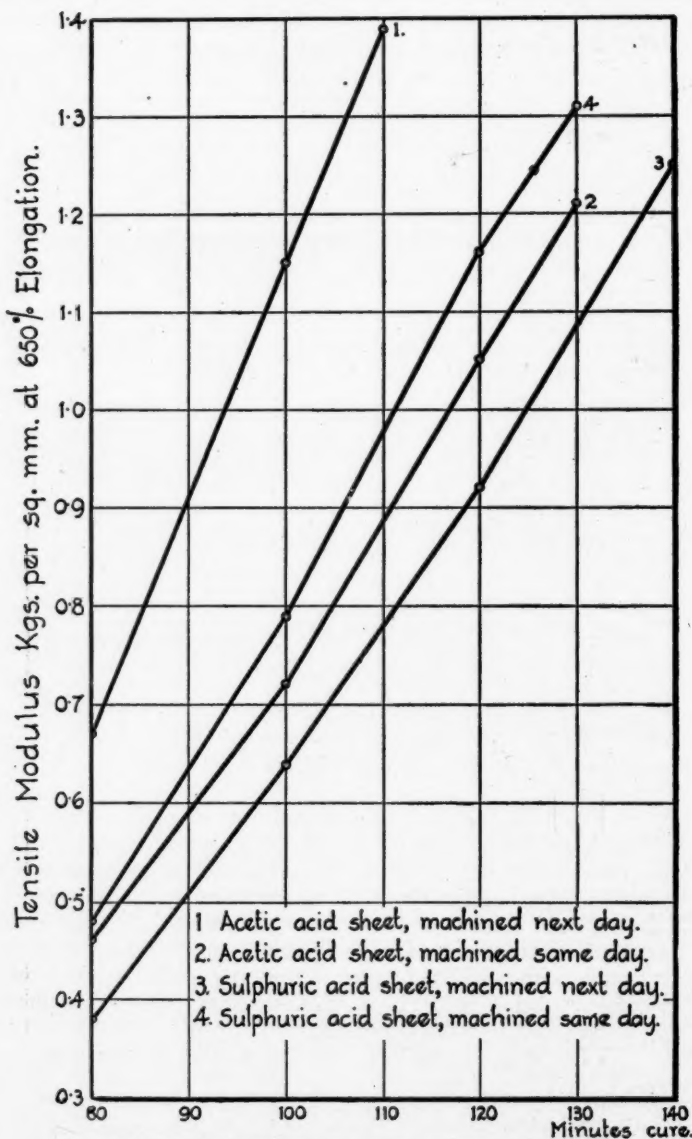


Figure 1—Vulcanization Properties of Air-Dried Sheet

ties, accompanied by thorough washing during machining, is not harmful to the resultant rubber.

The position with regard to use of sulfuric acid may now be summarized thus:

(1) Sulfuric acid gives satisfactory coagulation at a cost approximately one-half of that of formic acid and one-third of that of acetic acid.

(2) It is not harmful to the rubber provided that (a) it is used in the smallest possible quantity; (b) the sheet or crepe is washed with abundant water during machining.

(3) By the exercise of caution in the handling of the acid, the personal damages attendant on its use can be practically eliminated.

These conclusions may be somewhat amplified:

(1) The cost of sulfuric acid varies with the method of packing and with the quality. It will not be sufficient for a manager to ask his agents or his dealers merely for sulfuric acid without qualification. The acid purchased should be a good quality commercial grade, of specific gravity 1.84 (sometimes sold as 168° Twaddell). It will usually be found cheapest to purchase the acid in 2½ cwt. drums and not in glass bottles. The use of inferior grades of acid may cause trouble, and we recommend the use of only well-known British grades.

If the acid is of the above-mentioned gravity the figures given in this paper may be applied without further correction for purity. Estates purchasing more dilute acids are advised to submit samples to the R. R. I. for analysis.

(2) Estates commencing the use of sulfuric acid must be prepared to spend a week or two on experiments designed to determine the most satisfactory quantity of coagulant to use. For next-day machining, using a latex of 1½ lbs. (dry rubber), the figures mentioned previously may be taken as a starting-off point, *i. e.*, 2.66 grams per pound of dry rubber, or approximately 1 fluid ounce of acid per 20 pounds of dry rubber. The use of the smaller quantity shown in Table I, *i. e.*, 2.0 grams per pound or one fluid ounce to 26 pounds of dry rubber, may be found satisfactory for same-day machining, but this coagulum will be unduly tough and difficult to wash if left overnight.

(3) Safe handling of sulfuric acid is mainly a matter of common sense but certain cardinal points may be mentioned: (a) when diluting, the acid should always be added to water and not water to acid; (b) the addition should always be made slowly; (c) sulfuric acid should never be held above level of the eyes or poured in such a position that splashes could reach the eyes; (d) when moving sulfuric glass bottles containing sulfuric acid they should be held at the bottom and never at the top.

The acid must be added to the latex in very dilute solution, and the most convenient mixture is 50 fluid ounces of pure acid per 50 gallons of water. The number of fluid ounces of acid being added to any quantity of latex is then easily checked.

It is sometimes suggested that the safest method is for the manager to dilute the pure acid immediately after it is received at the factory. This method insures against unauthorized tampering with the acid in its most dangerous form. The acid may be only partially diluted at this stage—say to 30%—and then further diluted immediately before use. In a well-disciplined factory this preliminary dilution may be regarded as rather unnecessary.

If used in the minimum proportions, the sulfuric acid contained in the serum will not cause any great corrosion of the machines. It is essential, however, that after machining is completed, fresh water should be run over the rolls for some minutes to assure that the film of water which remains is quite free from acid. If this precaution is not observed, the evaporation which takes place during the day may leave on the rolls a very small quantity of a very concentrated acid, and the cumulative effect of this daily treatment may cause appreciable corrosion.

In conclusion it should be emphasized that in the use of sulfuric acid, considerations of cost, efficiency, and quality of products all point in the same direction. The lowest cost is obtained by using a minimum quantity of acid; this yields the softest coagulum; this in its turn facilitates washing and yields the thinnest and fastest drying sheet; the efficient washing is responsible for producing the fastest curing and least acid rubber.

Since writing the above certain facts have come to our notice which must be given due prominence in any discussion of the subject.

Several estates have recently experimented with sulfuric acid, and some have obtained satisfactory results almost immediately. Others, however, have experienced considerable difficulty in obtaining a satisfactory and consistent coagulation. The chief difficulty appears to have been bubble formation—at least partially caused by insufficient accuracy in the measurement of the acid and careless or unduly prolonged stirring. In most instances it has been found possible to overcome these difficulties, but it must be admitted that this coagulation is less easily controlled than the normal formic acid method. We again stress the fact that the manager turning over to sulfuric acid must expect to devote a certain amount of time to preliminary trials and errors.

The other outstanding fact is that some brokers and consumers still maintain their opposition. There is, of course, no uniformity of opinion on this point and, that sulfuric acid sheet is acceptable to some consumers, is shown by the fact that several estates have been selling such sheet at top price for many years.

The question may be settled for any particular seller by submitting preliminary samples of sulfuric acid sheet, prepared on a small scale, in the normal market. It is desirable, however, to quote in full the warning printed in the *Bulletin of the Rubber Growers' Association*, August, 1926, which, since it has not been revoked, presumably still represents the official opinion.

"A communication has been received recently from the Rubber Association of America intimating that at a meeting of the Board of Directors of that Association the matter of the use of sulfuric acid as a coagulant was considered. The question arose on account of the apprehensions expressed by a representative group of technical men with respect to probable harmful effect of sulfuric acid on the curing and aging qualities of rubber. The Directors of the Association share the apprehension of their technical men and ask the assistance of the Rubber Growers' Association in endeavoring to discourage and possibly eliminate sulfuric acid as a coagulating agent.

"It will be remembered that a warning against the use of sulfuric acid as a coagulant was published in the *Bulletin* for May, 1923, pp. 247-249, and it was then stated that the disadvantages attaching to this substance had been reported from time to time. It has been clearly shown that coagulation with sulfuric acid produces a rubber which cures more slowly than that prepared with acetic acid. Further, if more sulfuric acid is used than is necessary, the effect on the rate of cure of the rubber produced is much greater than it would be if a similar excess of acetic acid were employed. On most estates it is usual to employ a slight excess of acid over the minimum amount to assure a clean coagulation under all weather conditions, and consequently if sulfuric acid be used the slightest excess of acid necessary will be harmful. It may be of interest to recall the fact that sulfuric acid was only suggested as a makeshift during the war when supplies of acetic acid were not available. Sulfuric acid is a cheaper acid than acetic acid, and goes further, but the saving in cost does not warrant its use. It is possible that the use of sulfuric acid accounts for complaints from manufacturers as to the variability in the rate of cure of plantation rubber which continue to be received.

"Estate managers are strongly recommended to return to the use of acetic acid, or to utilize sodium silicofluoride or formic acid, as recommended in the *Bulletin* for September, 1925. Sulfuric acid is not recommended for coagulating latex."

This advice was given in 1926 and was probably very sound advice. It has been quoted to us in correspondence in 1932 when its soundness is more problematical. Conditions have changed very considerably in the intervening period, and several pertinent remarks may be made. In August, 1926, the price of rubber was one shilling and sixpence per pound, and the approximate costs of coagulating with acetic and sulfuric acids were 0.17 and 0.05 cent per pound, respectively. In 1932 the price of rubber is approximately twopence per pound, and the acid costs are not very different from those of 1926. The saving represented by sulfuric acid is now a very much larger percentage, both of the cost of production and of the margin between production cost and selling price. Again, methods of factory control have greatly improved and there now appears to be very little necessity for using more than the minimum quantity of acid, whatever coagulant is used. As regards the variability of plantation rubber there is much evidence to show that this is still considerable even among estates using only formic acid. The intelligent use of sulfuric would not increase this variability very greatly and, as far as each individual estate is concerned, the absolute necessity for the strictest control of the amount of acid used would probably lead to a more uniform product.

It is impossible for us definitely to recommend the use of sulfuric acid, since the varying requirements in different markets renders the problem as much commercial as technical. It is possible to produce a good quality rubber by the use of sulfuric acid, provided sufficient care is exercised, but even the best rubber thus produced may prove unwelcome if it falls into the hands of a buyer who has a fundamental and long-standing objection to the coagulant.

References

- ¹ Martin, *Rubber Industry*, p. 205 (1914).
- ² Eaton, *Agri. Bull. F. M. S.*, No. 27, 223 (1918).
- ³ De Vries, *Estate Rubber*, p. 176 (1920).
- ⁴ Morgan and Stevens, "Preparation of Plantation Rubber," p. 303 (1928).

The Electro-Deposition of Rubber from Revertex and Revultex

N. Budiloff

BERLIN

Up to the present time there have been only a few articles¹ on the electro-deposition of rubber from latex, whereas patents have continued to increase during the last ten years. They are based upon the fundamental observation of Henri,² who in 1907 proved that rubber particles in natural latex are negatively charged and that in an electric field they migrate to the anode.

Starting from this observation, Cockerill in 1908³ suggested the precipitation of rubber from latex on a moving platinized belt connected with the anode. Somewhat later, Clingnett⁴ substituted coagulation by acids on the plantations by electro-deposition. All these experiments were only for the purpose of obtaining raw rubber from latex. The first process for the production of rubber articles was developed and applied practically around 1923 by Klein and Szegvari⁵ on the one hand and by Sheppard and Eberlin⁶ on the other. Besides the deposition of pure rubber, these investigators succeeded in introducing fillers and colors into the latex and precipitating them simultaneously with the rubber on the anode.

Our problem was to investigate the possible use of concentrated latex (Revertex) and of vulcanized and concentrated latex (Revultex) in the production of finished rubber articles by electro-deposition directly on the metal.

It was difficult to find a serviceable method among the numerous patents. The work was rendered difficult by the fact that a large number of patents promised more than actually proved to be the case. The patent of the Anode Rubber Company⁷ was, however, found to be suited for our purpose.

The electrophoretic deposition of rubber from latex is carried out according to this patent with a current density such that the potential between the electrodes is less than 1.7 volts, which is insufficient to produce electrolysis with formation of gas. In the experiments, zinc was used for the anode and carbon for the cathode. The rubber layer was very uniform, non-

porous, coherent and of good quality. The anode was not attacked and after polishing it with emery it was used over again. This process was used as the essential procedure in subsequent work.

The electrical assembly for these experiments was as follows (see Fig. 1). In the first experiments a constant voltage of 1.5 volts was maintained. The current density varied though at the beginning it was not above 0.8 ampere per square decimeter. A dilute Revertex paste containing about 30 per cent rubber was used for the electrolyte. The original paste (rubber content about 60 per cent) was diluted with an equal volume of water. The dilution was carried out

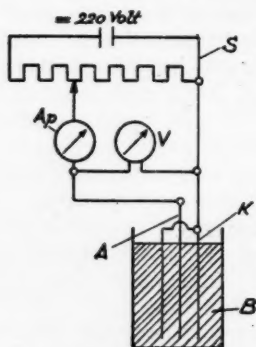
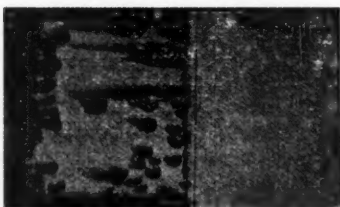


Figure 1—Arrangement of Apparatus

- S = resistance
- A_p = ammeter
- V = voltmeter
- K = carbon cathode
- A = anode (zinc, etc.)
- B = Revertex container



Photograph 1—Rubber Deposited from Reverter, without Ammonia, on a Zinc Anode



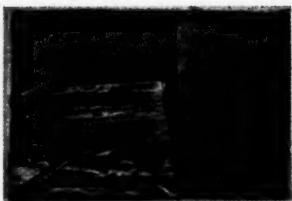
Photograph 2—Rubber Deposited from Reverter on a Zinc Anode, with Ammonia



Photograph 3—Rubber Deposited from Reverter, without Ammonia, on a Cadmium Anode



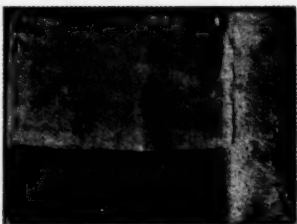
Photograph 4—Rubber Deposited from Reverter, without Ammonia, on an Iron Anode



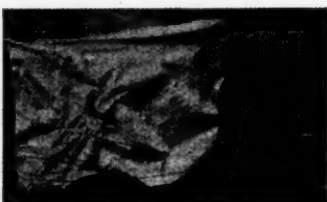
Photograph 5—Rubber Deposited from Reverter, without Ammonia, on a Lead Anode



Photograph 6—Rubber Deposited from Reverter with Ammonia, on a Tin Anode



Photograph 7—Rubber Deposited from Reverter with Ammonia on a Cadmium Anode



Photograph 8—Rubber Deposited from Reverter with Ammonia on an Iron Anode



Photograph 9—Rubber Deposited from Reverter with Ammonia on a Lead Anode

according to directions given by Hauser.³ To the paste was first added one-third of the necessary quantity of water, blended well, and let stand undisturbed about 0.5 hour, after which time the remaining two-thirds water was added, with agitation of the mass. After another 0.5 hour the Revertex paste was ready for use.

Microscopic and ultra-microscopic examination showed that dilute Revertex has no agglomerated particles and is well dispersed. The consistency of diluted Revertex is the same as that of latex preserved with ammonia. The first deposits were very different from those of latex. The rubber deposits from Revertex were not uniform; *i. e.*, were thick in places and thin in other places. (See Photograph 1.) The experiments were repeated a few times with the same results.

It is therefore impossible under the experimental conditions described to obtain good rubber articles from Revertex. In testing the method, ammonium chloride was added in the deposition of latex. It was found that upon the addition of only a few per cent of ammonia—to neutralize the acids formed—the previously irregular precipitates became smooth and uniform. Furthermore the excessive corrosion of the zinc anodes was diminished. Since it had been shown in the experiments with Revertex that here, too, the zinc anodes showed marked and uneven corrosion, experiments on the deposition of rubber from Revertex to which ammonium hydroxide was added were carried out.

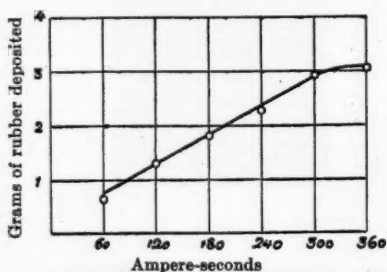


Figure 2—Relation between the Rubber Deposited and the Quantity of Electricity

The addition of even a small quantity of ammonium hydroxide completely changed the behavior of Revertex. Thus the addition of 2.5 cc. of ammonium hydroxide (d. 0.91) to 250 cc. of Revertex (diluted 1:1) gave a completely uniform non-porous coating which was very thin. With increasing quantities of ammonium hydroxide the polarization diminished perceptibly. Since the conductivity is increased by the addition of ammonium hydroxide, at a voltage of 1.5 volts more current passed through the electrolyte,

with formation of a thicker deposit of rubber. The addition of ammonium hydroxide is however limited because of the formation of froth on the cathode. With large quantities of ammonia the surface of the coating becomes covered with tiny bubbles which have the appearance of a sediment and lower the quality of the rubber greatly. The addition of 10 cc. of ammonium hydroxide (d. 0.91) to 250 cc. Revertex (1:1) gave the best results. After one hour of deposition the coating was about 1 to 2 mm. thick, was very uniform and was non-porous (see Photograph 2). Several substances other than ammonia were tested, as shown in Table I.

TABLE I

Addition	Remarks
1. Potassium hydroxide	Small quantities showed no improvement in the deposit Larger quantities (10 cc. of 0.10 <i>N</i> NH_4OH per 250 cc. Revertex or more) gave extremely thin coatings because of sudden stoppage of the current
2. Water glass	No improvement
3. Dimethylamine	No improvement
4. Trimethylamine	No improvement
5. Pyridine	No improvement

After it had been proved that a certain content of ammonium hydroxide in the Revertex is indispensable for the formation of good rubber coatings, further experiments were carried out to explain the phenomenon which takes place during the electro-deposition of rubber from Revertex.

1. First of all, the relation between the quantity of rubber deposited and the quantity of electricity consumed was studied. In these experiments, temperature, concentration, and conductivity were constant, under which conditions it was found that the quantity of rubber deposited was roughly proportional to the quantity of electricity.⁹

TABLE II (SEE FIG. 2)

THE RELATION BETWEEN THE QUANTITY OF RUBBER DEPOSITED AND THE QUANTITY OF ELECTRICITY

Current density, 0.1 amp. per sq. dm.

Conductivity, $77.5 \times 10^{-4} \frac{1}{\Omega \text{ cm.}}$

p_H , 11.6.
Temp., 18° C.

Electrolyte 250 cc. Revertex (diluted 1:1) + 10 cc. NH_4OH (d. 0.91).

Expt. No.	Time in Min.	Amperes	Rubber Deposited in G.
1	10	60	0.5894
2	20	120	1.2780
3	30	180	1.7672
4	40	240	2.3124
5	50	300	2.8784
6	60	360	2.9940

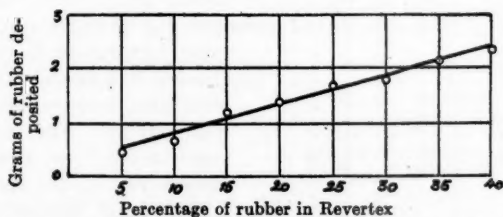


Figure 3—Relation between the Quantity of Rubber Deposited and the Rubber Content of Revertex

TABLE III (SEE FIG. 3)

THE RELATION BETWEEN THE QUANTITY OF RUBBER DEPOSITED AND THE CONCENTRATION

Current density, 0.1 amp. per sq. dm.

Duration, 30 min.

Temp., 18° C.

Expt. No.	Concentration of Rubber in Revertex	Rubber Deposited in G.
1	5	0.4562
2	10	0.7234
3	15	1.2030
4	20	1.3512
5	25	1.7045
6	30	1.8123
7	35	2.1985
8	40	2.4134

2. Secondly, is the quantity of rubber deposited proportional to the concentration of the rubber in Revertex?¹⁰

In addition, the influence of the current density on the deposition of rubber from Revertex was studied experimentally. As shown in Table IV, the deposition of rubber was studied from 0.02 up to 1.0 ampere per sq. dm. It was found that a current density of 0.1 ampere per sq. dm. gave the best yield.

TABLE IV (SEE FIG. 4)
RELATION BETWEEN THE QUANTITY OF RUBBER DEPOSITED AND THE CURRENT DENSITY
Current, 180 amperes per second.
Conductivity, $108 \times 10^{-4} \frac{1}{\Omega \text{ cm.}}$

Experiment No.	Current Density in Amp./Sq. Dm.	Duration of Expt.	Quantity of Rubber Deposited in G.
1	0.02	150	0.7464
2	0.04	75	1.3592
3	0.06	50	3.6592
4	0.08	37.5	3.8084
5	0.10	30	4.0360
6	0.20	15	3.4708
7	0.40	7.5	2.9100
8	0.60	5.0	2.5412
9	0.80	3.75	2.4130
10	1.00	3.0	2.4020

The yield of rubber per faraday can be increased in the following ways.

1. If a current is conducted through the electrolytes for a long time, is then interrupted, and the zinc anode left for a short time in the Revertex without any current, the quantity of rubber deposited increases, just as Herrmann (Physikochem-

ische Laboratorium of Siemens and Halske) has already shown to be true with latex suspensions (private communication). For example, by passage for 0.5 hour of a current of 0.1 ampere per sq. dm. through Revertex, 1.4960 g. of rubber were deposited (average of five experiments). On the contrary, when the zinc anode was allowed to stand in the suspension without any current for another 0.5 hour, the quantity of rubber obtained increased to 1.9040 g., i. e., approx. 27

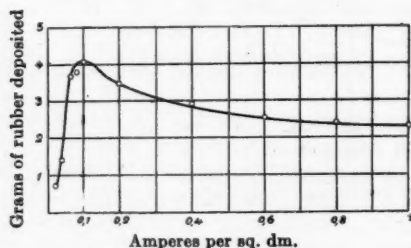


Figure 4—Relation between the Quantity of Rubber Deposited and the Current Density

per cent. The quantity of rubber deposited therefore increased with immersion of the anode without any current.

2. By the addition of electrolytes, of which ammonium acetate is the best, the yield of rubber increases with increase in the electrolyte until at a content of 4.5 per cent of ammonium acetate (calculated on the liquid Revertex) spontaneous coagulation takes place, not only in the immediate vicinity of the zinc anode but throughout almost the entire bath.

In connection with this experiment, it should be mentioned that the water content of the film of rubber deposited increases with increase in the quantity of ammonium acetate (see Table V and Fig. 6). All these facts indicate that in the electro-deposition of rubber a secondary process at the electrodes is involved. Based

on the work of Sheppard¹⁰ the deposition can be explained in the following way. During the passage of the current, zinc dissolves in the anode with formation of zinc ions. The concentration of rubber in the vicinity of the anode is increased by electrophoretic migration. The zinc ions formed at the electrode then coagulate the rubber particles. The coagulated rubber particles form a diaphragm through which passes the liquid electrolyte, so that no interruption of the current takes place. If the current is then interrupted, the electrophoretic migration of the rubber particles immediately stops, while the zinc ions in solution move forward toward the suspension, and coming in contact with the rubber particles, flocculate the latter out of the suspension. In this way the influence of added salts, such as ammonium acetate, can be explained easily. At the anode the acid ions which have accumulated by electrolytic migration have a coagulating effect over and above that of the zinc ions already present.

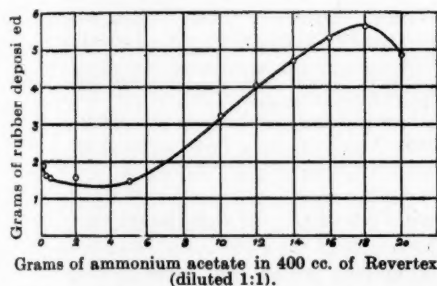


Figure 5—Relation between the Quantity of Rubber Deposited and Ammonium Acetate Added

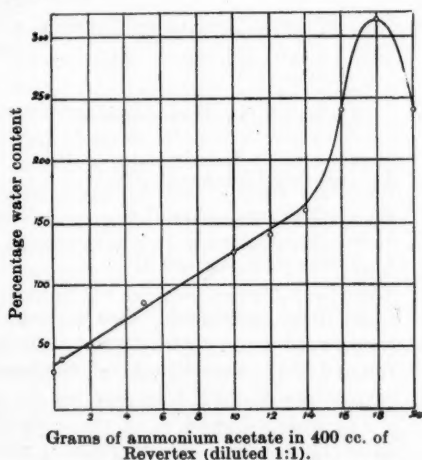


Figure 6—Percentage of Water in the Deposited and Dried Film for Different Quantities of Ammonium Acetate Added

TABLE V (SEE FIG. 5)
RELATION BETWEEN THE QUANTITY OF RUBBER DEPOSITED AND THE QUANTITY OF AMMONIUM ACETATE CONSUMED

Current density, 0.1 ampere per sq. dm.
Duration, 30 min.
Temp., 20° C.

Expt. No.	Ammonium Acetate in G. per 400 Cc. Revertex	Quantity of Rubber Deposited (in G.)	Conductivity α cm.	pH	Water Content of the Dried Rubber in %
1	0.1	1.8700			...
2	0.2	1.6290			...
3	0.5	1.6090			40
4	2.0	1.5960			51
5	5.0	1.4256			85
6	10.0	3.2500			125
7	12.0	4.0360			140
8	14.0	4.7162			160
9	16.0	5.3098	180×10^{-4}	9.4	240
10	18.0	5.6500	235×10^{-4}		314
11	20.0	4.9300			240

Without the addition of ammonium acetate the rubber deposited had a water content of 30 per cent.

General Behavior of Metal Anodes during the Deposition of Rubber

In the deposition of rubber directly on metal, the nature of the metal obviously plays an important part. In order to study the suitability of different metals for the electro-deposition of rubber, experiments were carried out with zinc, cadmium, iron, lead, and tin. Because of its destructive action upon rubber, copper was not included in the investigation. The destructive action of copper and its salts on raw and vulcanized rubber has been known for a long time, and has been described by Dewar, Thompson and Lewis,¹¹ Weber,¹² and Morgan.¹³

The experiments were carried out with Revertex (diluted 1:1) with and without the addition of ammonia. Without exception, all metals without ammonia gave wholly useless coatings. Table VI gives a summary of the effects.

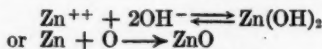
TABLE VI
DEPOSITION OF RUBBER ON DIFFERENT METALLIC ANODES FROM REVERTEX WITHOUT AMMONIA

Metal	Deposition
1. Zinc (see Photograph 1) Cadmium (see Photograph 3)	Not uniform, non-homogeneous, and non-coherent. After one hour with a current density of 0.1 amp. per sq. dm. it was 1 mm. thick
2. Iron (see Photograph 4)	Non-coherent and strongly colored by the added ferrous oxide
3. Lead (see Photograph 5)	Coherent but uneven coatings about 0.2 mm. thick
4. Tin (see Photograph 6)	Non-coherent coatings about 0.1 mm. thick

All these experiments were carried out with 1.5 volts. In experiments 2 to 4, the current density varied greatly during the course of the experiment, and toward the end of the experiments fell to about 0.02 ampere per sq. dm., after an original current density of 0.1 ampere per sq. dm.

The addition of 10 cc. of ammonia (d. 0.91) to 250 cc. of Revertex (diluted 1:1) gave (1) with zinc (Photograph 2) and Cd (Photograph 7) good, uniform, homogeneous, non-porous coatings which were about 1 mm. thick at the end of an hour; (2) with lead (Photograph 9) uniform, but very thin coatings; (3) with tin (Photograph 10) the same coatings as without any addition of ammonia; (4) with nickel in both cases very thin films which became tacky after about one month.¹⁴

A consideration of the anodic behavior of zinc, cadmium, iron, lead, and tin in weak alkaline liquids and liquids containing colloids such as Revertex will make clear the behavior of metals during the anodic deposition of rubber from Revertex. In the anodic solution of zinc at the anode, zinc ions go into solution, and OH ions migrate to the anode from the solution, so that the following reaction takes place:



The alkalinity at the anode is not sufficiently great to dissolve the zinc oxide formed. Consequently the anode becomes covered with an insoluble insulating layer of zinc oxide. Since the zinc does not dissolve wholly uniformly (partly on account of the irregular structure formed in the rolling of the metal), at some places the layer of zinc oxide is protected, whereas in other places the zinc ions can still go into solution. At the same time contact of the electrolyte with the anode becomes confined to a more or less restricted surface. For this reason, the further deposition of rubber takes place only at the soluble places, and irregular deposition results. Exactly the same thing happens in the case of the cadmium anode. The alkalinity

is increased by the addition of ammonia. Zinc oxide dissolves. The electrolyte comes in contact with the whole surface, and the deposited rubber coats the electrode uniformly. Tin goes into solution as stannous ions in weakly alkaline medium upon application of an external voltage. Since, however, stannous oxide is soluble only to a limited extent in this medium, it deposits on the anode when the electrolysis is prolonged. A resistance is set up in this way, and the strength of the current becomes very low, so that no significant quantity of rubber can be deposited.

With lead anodes, lead dioxide is formed on the surface of the anode during passage of the current. This is difficultly soluble in ammonia and requires a higher decomposition voltage; accordingly on this account only very thin rubber coatings are formed.

Introduction of Fillers

Pure rubber, *i. e.*, rubber without addition of sulfur or fillers, has only a very limited use in practice. For this reason the attempt was made to deposit rubber, sulfur, and other fillers simultaneously. Naturally only materials which have the same negative charge as the rubber in Revertex were used.

As a beginning, the problem of the introduction of sulfur into rubber was studied. In the first experiments, the precipitated rubber films were afterward immersed in ammonium polysulfide. Under these conditions the sulfur was unevenly dispersed, as is shown in the following example. A freshly separated deposit was dried in air for 10 minutes, and with its zinc base was immersed in yellow ammonium sulfide containing 10 per cent of sulfur. After 15 minutes in the solution the film was washed with water, dried, and different sections of the sample were analyzed, with the following results.

TABLE VII
INTRODUCTION OF SULFUR BY IMMERSION IN POLYSULFIDE

Sample No.	Experiment XX, % Sulfur	Experiment XXI, % Sulfur
1	6.04	3.06
2	5.55	3.63
3	7.00	2.13
4	3.86	1.91
5	..	4.28

Because of the nature of these results, the method described above was abandoned, and instead the polysulfide was mixed with the Revertex and the electro-deposition carried out at the same time.

Even small additions of 10 per cent of ammonium polysulfide solution to dilute Revertex (1:1) gave extremely poor results. The deposited rubber coating was streaked and uneven with 1 per cent of sulfur (based on 100 parts rubber in Revertex), as was the case with 2, 3, and 4 per cent of sulfur. With 5 per cent of sulfur the deposit was extremely thin and could hardly be removed from the metal. The experiment was repeated as a control, and the same results were obtained each time. It is believed that these phenomena can be explained in the following way.

The deposits obtained by the addition of polysulfide were not very thick, and they became thinner with increase in the sulfur content. It may therefore be supposed that the zinc sulfide which was formed made a resistant layer on the electrode. Colloidal sulfur was not used, since it is too expensive for technical use.

In addition experiments were carried out with finely ground crystallized sulfur with an average diameter of about $1\ \mu$. When the finely divided sulfur was mixed

with diluted Revertex (1:1), the sulfur precipitated out after a short time. This disadvantage can be overcome in three ways. The rate of sedimentation of solid particles in a liquid follows Stokes' Law:

$$v = \frac{2}{9} g \frac{(D - DF)r^2}{\eta}$$

where g is earth acceleration, r the radius of the particles, η the viscosity of the dispersing agent, D the density of the dispersed phase, and DF the density of the dispersing agent.

The rate of sedimentation of the dispersed phase can only be diminished by: (1) decreasing the radius of the particles; (2) decreasing the specific gravity of the dispersed phase, and (3) increasing the viscosity of the dispersing agent.

The British Patent of Klein and Szegvari¹⁵ is based on method 2. According to this, pulverized sulfur is mixed with black or finely divided kieselguhr, and heated above the melting point of sulfur, then milled finely, and the Revertex added. Other fillers can be used in a similar way.

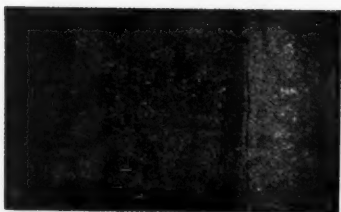
The same results were obtained by an increase in the viscosity. By the addition of a "protective agent," it is possible to introduce larger quantities of sulfur into Revertex very easily (over 50 per cent of sulfur, calculated on the rubber content in Revertex). The suspension was prepared as follows: 5 grams of sulfur, 2 grams of zinc oxide, 3 grams of protective agent to which 5 drops of ammonium ricinoleate¹⁶ and 12 cc. of aqueous ammonia had been added, were mixed together with 40 cc. of water, and to this mixture 300 cc. of Revertex (dilution 1:1) were added. The ammonium ricinoleate serves to increase the wetting of the sulfur and of the filler by the aqueous solution. The zinc oxide is used as activator for the accelerator during vulcanization. The suspension remains stable and keeps over half a year without the sulfur precipitating out. Upon analysis the coatings obtained from this suspension gave good agreement between the sulfur values in the film and in the suspension. In all cases the sulfur was uniformly distributed in the coating and the percentage of sulfur in the suspension and in the coating varied by only a few tenths (see Table VIII).

TABLE VIII
SULFUR CONTENT IN THE SUSPENSION AND IN THE FILM

Expt. No.	Original Quantity of Sulfur in Per Cent	Quantity of Sulfur Found in Per Cent
1	3.4	3.22
2	3.94	3.86
3	3.66	3.26
4	6.7	6.1
5	4.2	3.7
6	4.0	3.96
7	50.0	50.0

Vulcanization of these samples can be carried out in the usual way or even better (since the films are only 1 to 2 mm. thick) by the use of Vulkacit P (piperidinium pentamethylenedithiocarbamate) of I. G. Farbenindustrie A.-G. by treating the deposit for about 30-35 min. at 85° C. in a 50 per cent aqueous solution of accelerator.

Besides sulfur, other fillers can be introduced in this manner, such as clay, chalk, carbon black, or zinc oxide, in fairly large quantities, as well as all kinds of coloring agents, such as ultramarine, Turkey red, red iron oxide, golden antimony sulfide, etc. With these mixtures it is possible to precipitate uniform deposits of rubber



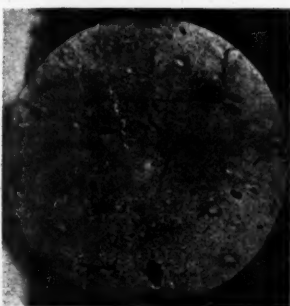
Photograph 10—Rubber Deposited from Reverex with Ammonia on a Tin Anode



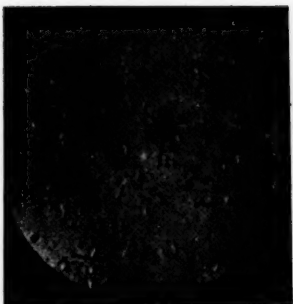
Photograph 11—Deposit of Rubber from Ammoniacal Reverex, Containing Chalk, on a Zinc Anode



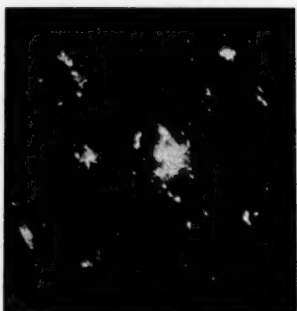
Photograph 12—Deposit of Rubber from Reverex, Containing Ammonia, Sulfur, Chalk, and Ultramarine, on a Zinc Anode



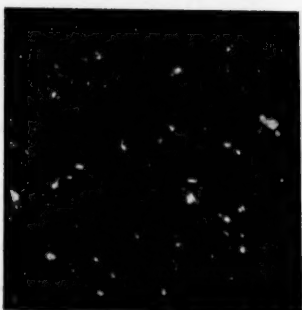
Photograph 13—Photomicrograph of Rubber Containing No Ammonia



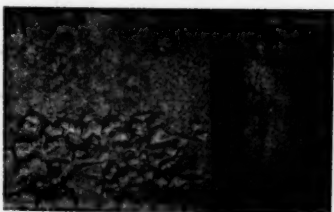
Photograph 14—Photomicrograph of Rubber, Containing Ammonia



Photograph 15—Ultra-photomicrograph of Rubber without Ammonia



Photograph 16—Ultra-photomicrograph of Rubber Containing Ammonia



Photograph 17—Rubber Deposited on a Zinc Anode from Reverex without Ammonia

(see Photographs 11 and 12). The compositions of the deposit and of the solution agree well with one another, and this is of great importance in two ways, first, because rubber with a definite filler content can be calculated in advance, and secondly, because otherwise the bath would soon become unusable through enrichment or impoverishment of filler.

Addition	SUSPENSION	
	Ash Calculated on 100 Parts of Rubber	Ash Found in the Rubber Deposit
4 g. zinc oxide	1.67 g. zinc oxide	
8 g. sulfur	4.17 g. sulfur	
5 g. protective agent	3.6 g. protective agent	
20 cc. ammonia (d. 0.91)		
5 drops ammonium ricinoleate		
25 g. chalk	16.68 g. chalk	
70 cc. water	0.68 g. calcium oxide	
500 cc. Revertex (diluted 1:1)	0.7 g. ash in Revertex	
	15.65% ash	16.38% ash

The somewhat higher ash content in the deposit becomes somewhat smaller if account is taken of the fact that zinc oxide is carried into the deposit by the electric current.

In conclusion, a few results of mechanical tests are given, which were carried out on rubber sheets from suspensions containing about 20–30 per cent of filler.

TABLE IX
Tensile Strength
(Kg. per Sq. Cm.)

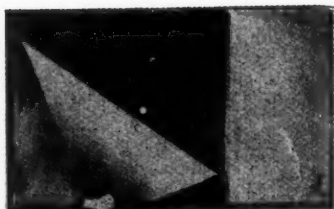
Expt. No.	Tensile Strength (Kg. per Sq. Cm.)	Percentage Elongation at Rupture
14	60	472
15	59	483
16	41	523
17	44	457
18	65	523

Experiments with Revertex

In addition to the experiments with Revertex, similar experiments were also carried out with Revultex. The vulcanized concentrated latex, Revultex, is of interest from the point of view that later vulcanization is avoided, so that all equipment for carrying out this operation can be dispensed with.

A series of experiments was first made in order to determine the most favorable conditions for the deposition of rubber from Revultex. A diluted Revultex containing about 30 per cent of rubber was used. The Revultex paste was diluted as in the case of Revertex just described. After dilution, microscopic and ultramicroscopic examination showed great differences between Revertex, latex, and Revultex. Whereas latex and Revertex particles are completely peptized, Revultex shows a large number of particles in the coagulated state (Photograph 13 is a microscopic picture of Revultex without the addition of ammonia). After the addition of ammonia, both microscopic and ultramicroscopic examination (Photographs 15 and 16, respectively) of Revultex showed noticeable differences from the original product. It appears as if the number of flocculated particles is decreased by peptization.

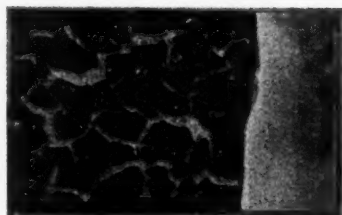
The experiments were carried out in the same way as with Revertex. Zinc, cadmium, iron, lead, and tin were used as anode, with carbon for the cathode. The voltage at the binding posts was 1.5 volts, and the experiment lasted one hour at a temperature of 20° C. The first layer deposited from Revultex without the addition of ammonia was not at all uniform (Photograph 17). After drying at room



Photograph 18—
Rubber Deposited on
a Zinc Anode from Re-
vulter Containing
Ammonia



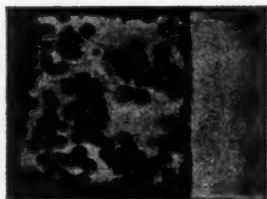
Photograph 19—
Rubber Deposited on
a Zinc Anode from an
Ammoniacal Revulter
Containing Carbon
Black



Photograph 20—
Rubber Deposited on
a Zinc Anode from an
Ammoniacal Revulter
Containing Fillers



Photograph 21—
Rubber Zinc Deposited
on a Zinc Anode from
an Ammoniacal
Revulter Contain-
ing Cadmium Yel-
low



Photograph 22—
Rubber Deposited
on a Zinc Anode
from a Revulter with-
out Ammonia



Photograph 23—
Rubber Deposited on
an Iron Anode from
a Revulter without Am-
monia



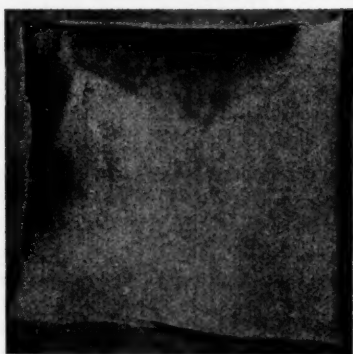
Photograph 24—
Rubber Deposited
on a Lead Anode
from a Revulter with-
out Ammonia



Photograph 25—
Rubber Deposited
on a Cadmium Anode
from a Revulter con-
taining Ammonia



Photograph 26—
Rubber Deposited
on a Lead Anode
from a Revulter con-
taining Ammonia



Photograph 27—Rubber Deposited
from Ammoniacal Revulter Contain-
ing Lithopone, and the Film Re-
moved before Drying

temperature it cracked in all directions. The addition of one cc. of ammonia immediately altered the behavior of the deposited rubber. The layer deposited was in fact very thin but uniform, and on drying it no longer cracked (Photograph 18). With increasing additions of ammonia, the deposits became thicker. The quantity of ammonia added was increased up to 15 cc. per 250 cc. of Revultex (diluted 1:1). Larger quantities are of no further value, since the violent evolution of ammonia causes frothing and the surface of the rubber is covered with fine bubbles, which affect its good appearance.

The introduction of fillers in Revultex offers no difficulties. On the other hand, when Revultex (diluted 1:1) containing fillers is used for the anodic deposition, the deposits crack in general on drying (Photograph 20) in spite of the addition of ammonia. On the other hand, diluted Revultex (1:1) gave with carbon black up to 20 per cent or mixed with the necessary quantities of colors, good, smooth, and non-cracking deposits (Photograph 21). As coloring agents, turkey red, cadmium yellow, and ultramarine were tested. The anodic behavior of metals during the deposition of rubber from Revultex was also studied. Zinc, cadmium, iron, lead, and tin were used as the anode in the deposition.

The experiments were carried out with and without the addition of ammonia. Without the addition of ammonia all the metals gave wholly unsatisfactory coatings, those with zinc (Photograph 21), cadmium (Photograph 22) were not uniform and cracked on drying. Iron (Photograph 23) gave coatings which were non-coherent, highly colored, and unsatisfactory. Lead (Photograph 24) gave coherent, non-cracking and very thin deposits which were not uniform. Similar unsatisfactory deposits were obtained with tin.

The addition of ammonia to Revultex altered the quality of the rubber deposited greatly, as is seen in the following table.

The table shows that among the metals studied only zinc and cadmium are to be considered for an anode in the preparation of finished vulcanized rubber articles from Revultex.

TABLE X
BEHAVIOR OF DIFFERENT METAL ANODES IN REVULTEX WITH THE ADDITION OF AMMONIA

Metals	Appearance
Zinc (Photograph 18) }	Uniform, coatings which did not crack on drying
Cadmium (Photograph 25) }	
Iron	Thin, uniform coatings not colored by iron
Lead (Photograph 26)	The same
Tin	Very thin coatings, exactly like those without the addition of ammonia

The addition of ammonia in general appears to cause a fundamental structural change in the rubber deposited from Revultex and Revertex, which can be distinctly seen by the experiment described below. It was found that when rubber deposited on porous forms, either electrically or by immersion, was swollen in water, the rubber deposited without the addition of ammonia swelled sixty times as much as it did when it had been deposited in the presence of ammonia. If the rubber is prepared without ammonia it can after 24 hours' immersion in water be very easily compressed and crumbled between the fingers. It is then white and opaque in appearance.¹⁷ The rubber with the addition of ammonia is firm, elastic, no longer compressible, has a yellow or brown color, and is transparent. Furthermore, it is worthy of note that the linear shrinkage is reduced from 20 to 5 per cent by the addition of ammonia.

This also explains why deposits from Revultex prepared without ammonia show considerable cracking on drying. In what way the structural change is to be explained in the individual cases is impossible to decide with the experimental material so far available.

It is immaterial what serves as the binding agent of the rubber particle, whether protein or resinous compounds as Hauser¹⁸ assumes, or whether the rubber hydrocarbon¹⁹ itself is regarded as the binding agent. The fact remains that the adhesive force between the individual rubber particles is greatly diminished by vulcanization. Upon drying a very great stress is set up, and the binding agent no longer withstands this tension, and the whole coating cracks. Upon the addition of ammonia the tension, as can be concluded from the results of the experiments, is reduced, and the coating withstands the lower tension successfully. If the coating obtained without the addition of ammonia is carefully removed from the metal form before drying and is then dried, it remains intact (Photograph 27).

Summary

1. It was found that to obtain satisfactory deposits at the anode from Revertex, a certain quantity of ammonia must be added to the Revertex.
2. It was found that the quantity of rubber deposited depends upon the quantity of electricity, the current density, and upon the concentration of rubber in the Revertex.
3. It was found that, among the metals studied, only zinc and cadmium or metals coated with zinc can be used for the anode.
4. The problem of obtaining on the anode faultless rubber deposits from diluted Revertex (1:1) after the addition of sulfur and fillers was solved. On the contrary, it was not possible to obtain satisfactory deposits at the anode from dilute Revultex containing fillers, with the exception of carbon black and coloring agents.

References

- ¹ Sheppard and Eberlin, *Ind. Eng. Chem.*, **17**, 711 (1923); Elliot, *Chem. Met. Eng.*, **33**, 358 (1926); Baclesse, *Kautschuk*, **3**, 67 (1926); Sheppard, *Trans. Am. Electrochem. Soc.*, **52**, 47 (1927); Klein, *Rubber Age* (London), **9**, 365 (1928); Johnston and MacKay, *Rev. gen. Caoutchouc*, **8**, 146 (1931).
- ² Henri, *Soc. Biol. Paris*, **13** (1906); *Compt. rend.*, **144**, 431 (1907); *Lecture on Rubber*, 203-206 (1908).
- ³ Cockerill, English Patent 21,441 (1908); 5854 (1910).
- ⁴ Clingnett, *Rub. Rec.*, **1914**, 374.
- ⁵ Klein and Szegvari, English Patent 223,188 (1923).
- ⁶ Sheppard and Eberlin, U. S. Patent 1,476,374 (1923).
- ⁷ Anode Rubber Co. (Klein), English Patent 316,504 (1928).
- ⁸ Hauser, *Kautschuk*, **3**, 2 (1927).
- ⁹ Klein obtained the same results with a deposit of rubber from latex on zinc anodes; *Trans. Inst. Rubber Ind.*, **1929**, 347; Sheppard, *Trans. Am. Electrochem. Soc.*, **52**, 47 (1927).
- ¹⁰ Sheppard, *Trans. Am. Electrochem. Soc.*, **52**, 47 (1927); Klein, *Trans. Inst. Rubber Ind.*, **1928**, 349.
- ¹¹ *Kautschuk*, **7**, 42 (1931).
- ¹² *J. Soc. Chem. Ind.*, **19**, 546 (1900).
- ¹³ *Preparation of Plantation Rubber*, page 164.
- ¹⁴ Stevens, *Latex*, **1928**, page 30.
- ¹⁵ English Patent 254,765 (February, 1925).
- ¹⁶ Ammonia ricinoleate was used on the recommendation of Overbeck (Continental Gummi-Werke A.-G. Hannover).
- ¹⁷ See also *Gummi-Ztg.*, **43**, 2325 (1929).
- ¹⁸ *Latex*, page 131.
- ¹⁹ Von Weimarn, *Kolloid-Z.*, **46**, 217, 223 (1928).

The State of Rubber in Solutions

Part II. The Effect of the Temperature on the Viscosity of Solutions of Various Concentrations

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The previous communication¹ dealt with the isotherm of the surface tension of a rubber-benzene solution at the boundary of water; in the range of concentration the minimum of the isotherm was 0.3 to 0.6 per cent. From this it was concluded that the descending branch of the isotherm corresponds to the molecular state of rubber in the solution, whereas the ascending branch corresponds to the micellar state. The conversion of a molecular to a micellar solution is accompanied by changes in a series of viscometric phenomena, as has been established by several investigators. In particular it was found that deviations from the Einstein and the Hagen-Poiseuille laws occur in rubber solutions at those concentrations which correspond to the minimum of the isotherm of the surface tension. In connection with the work of Staudinger,² which is so closely related to the subject and which deals with differences in the values of the viscosity-temperature coefficients of molecular and micellar solutions, it appeared to us of interest to prove the coincidence of the isotherm minimum of the surface tension with the temperature change in the viscosity coefficient.

As Haller³ has already pointed out, the data on the influence of temperature upon the viscosity are contradictory to a certain degree. According to measurements by Abernethy⁴ and Dogadkin and Pewsner⁵ the relative viscosity diminishes with increase in temperature. On the contrary Haller⁶ and Whitby⁷ reported positive viscosity-temperature coefficients of rubber solutions. This contradiction is, according to our opinion, related to the fact that the measurements by the various authors are carried out with solutions of different concentration. Haller and Whitby carried out viscosity measurements with solutions having a rubber content of not more than 0.65 g. per 100 cc., whereas Abernethy and Dogadkin and Pewsner employed higher concentrations. In this way the change in sign of the temperature coefficient may depend upon the state of the rubber used in the experiments. Direct evidence of this is to be found in Haller's quantitative data; several solutions with a concentration of less than 0.33 per cent showed an increase in the relative viscosity with an increase in temperature, whereas solutions with concentrations of 0.65 per cent showed a diminution in the viscosity. In Haller's experiment the change in sign of the viscosity-temperature coefficient corresponds exactly to that range of concentration where, according to our measurements, the minimum in the isotherm of the surface tension occurs. Further experiments should confirm this conclusion.

I. Experimental Part

The measurements were carried out in capillary viscometers of special construction which were designed to prevent evaporation of the solvent. Hatschek's book⁸ has a description of such a viscometer. The rate of flow of the solvent was calculated graphically from a curve representing a series of measurements within the temperature range. By means of a dilatometer it was proved that the coefficient of expansion of the solvents (benzene and xylene) and of the solutions at the concentrations tested is one and the same; their density is also the same.

On this basis the relative viscosity was calculated according to the simplified formula:

$$\eta = \frac{T \text{ of the solution}}{T \text{ of the solvent}}$$

The viscosimeters were calibrated in such a way that the Hagen-Poiseuille law was valid.

In order to prevent any influence of oxygen on the rubber, some of the measurements were carried out in an atmosphere of carbon dioxide; the solvent was also aerated with carbon dioxide. It was expected that repeated passage through the capillary tube of the viscometer under the influence of purely mechanical effects on the rubber (milling) would lead to a diminution in the viscosity; consequently experiments were carried out in which the measurements were made with fresh portions of solutions each time. However these experiments showed that in this range of concentration such a diminution in the viscosity did not occur. Because of this, the measurements were for the most part carried out with a single portion of the solution, which was carried over from one thermostat to another.

Pale crepe, both unpurified and previously extracted with cold acetone in air and in an atmosphere of carbon dioxide, was used in the experiments. Small pieces of rubber were dried in a current of carbon dioxide and dissolved in dark glass receptacles containing xylene or benzene. These were agitated. The measurements were carried out on solutions which had been poured off from the undissolved rubber portion (rubber solution of the lighter fractions). In addition the viscosity measurements were carried out on a one per cent solution which had been irradiated for two hours with a quartz lamp in an atmosphere of carbon dioxide.

The results of the measurements are given in the following tables.

TABLE I
VISCOSITIES OF XYLENE SOLUTIONS OF UNPURIFIED PALE CREPE. MEASUREMENTS CARRIED OUT IN AIR

Concentration: 0.2%		0.4%		0.6%		0.8%		Calculated η According to the Formula: $\eta = 15.6 -$ $0.06t$
Tempera- ture in ° C.	η	Tempera- ture in ° C.	η	Tempera- ture in ° C.	η	Tempera- ture in ° C.	η Found	
5.2	2.43	6.5	4.35	3.2	10.19	5.8	15.12	15.20
10.8	2.44	12.5	4.29	15.5	9.57	14.5	14.58	14.54
23.2	2.42	20.8	4.20	22.5	9.41	24.5	13.90	13.91
35.0	2.39	41.2	3.90	44.8	8.56	39.0	13.28	12.91
59.0	2.36	62.5	3.64	59.2	7.94	59.0	11.50	11.53

TABLE II
VISCOSITIES OF BENZENE SOLUTIONS OF ACETONE-EXTRACTED PALE CREPE. MEASUREMENTS WERE CARRIED OUT IN AN ATMOSPHERE OF CARBON DIOXIDE

Concentration: 0.1%		0.2%		0.3%		0.4%		Calculated by $\eta =$ 4.9 - 0.029t
Tempera- ture in ° C.	η	Tempera- ture in ° C.	η	Tempera- ture in ° C.	η	Tempera- ture in ° C.	η Found	
16.0	2.07	11.5	2.5	10.8	3.89	10.5	4.68	4.70
27.2	2.00	26.0	2.44	26.2	3.85	26.0	4.25	4.39
35.5	2.00	30.5	2.46	31.0	3.78	31.0	4.24	4.29
40.5	1.99	40.5	2.44	36.0	3.70	36.0	4.18	4.18
45.5	2.00	48.0	2.42	42.0	3.70	47.0	4.00	3.96
55.5	1.99	48.0	3.75

0.56%			0.8%		
Temperature in ° C.	η Found	Calculated by $\eta = 7.15 - 0.029t$	Temperature in ° C.	η Found	Calculated by $\eta = 15.08 - 0.084t$
10.5	7.10	6.86	15.0	14.60	14.69
26.2	6.40	6.40	27.8	13.50	13.56
40.5	6.00	5.99	35.5	13.00	12.95
49.0	5.80	5.78	40.5	12.60	12.56
..	45.0	12.50	12.20
..	49.5	12.00	11.91

TABLE III

VISCOSITIES OF BENZENE SOLUTIONS OF PALE CREPE EXTRACTED WITH ACETONE IN AN ATMOSPHERE OF CARBON DIOXIDE. MEASUREMENTS CARRIED OUT IN AN ATMOSPHERE OF CARBON DIOXIDE

Concentration: 0.27%		0.47%		
Temperature, ° C.	η	Temperature, ° C.	η Found	η Calculated According to the Formula $10.2 - 0.061t$
17.0	4.49	17.0	9.21	9.16
25.6	4.48	25.6	8.64	8.60
34.0	4.46	33.7	8.26	8.15
44.0	4.48	39.8	7.80	7.77

TABLE IV

VISCOSITIES OF A ONE PER CENT XYLENE SOLUTION OF UNPURIFIED PALE CREPE IRRADIATED WITH A QUARTZ LAMP FOR 2 HOURS IN AN ATMOSPHERE OF CARBON DIOXIDE

Temperature, ° C.	η
3.5	1.86
10.5	1.66
22.5	1.50
39.0	1.50
59.8	1.46

II. Examination of the Results

It is evident from the tables that the relative viscosity of solutions of unpurified pale crepe in all the measurements diminished with increase in temperature for the concentrations studied. As for the acetone-extracted, resin-free rubber this decrease was apparent only in solutions containing over 0.3 per cent of dried substance. In solutions of lower concentration, however, the relative viscosity did not vary with change in temperature. This difference in the behavior of the two rubber samples is probably to be attributed to the degree of purity of the preparations; also it is to be attributed to the fact that the solutions of unpurified rubber were exposed to the depolymerizing influence of oxygen during the measurements in air.

The temperature characteristic of the viscosity of solutions of purified rubber consequently depends upon their concentration and evidently also upon the state of the rubber which they contain. On the assumption that molecular solutions of rubber are characterized by unchanging viscosity, the limiting concentration of such solutions is around 0.3 per cent. This value is close to that obtained by Staudinger,⁹ but it is somewhat different from the isotherm minimum of the surface tension, the average value of which is 0.5 per cent. However this imperfect agreement may be explained by the fact that the limiting concentration obtained from viscometric data establishes a sharper demarcation for molecular solutions than does the isotherm of the surface tension.

The fact that the viscosity is independent of the temperature at concentrations corresponding to the descending branch of the isotherm of the surface tension is a new proof that at these concentrations the rubber is in a state of molecular dispersion. This conclusion is to a certain extent supported by the closely related fact that the relative viscosity of solutions of electrolytes and substances not associated with them increases in most cases rather than diminishes with increase in the temperature. Furthermore, there are very good reasons for the lack of variations in the viscosity with the temperature of molecular solutions of rubber and of the condition of solvation of the molecules of these solutions. Since the solvation of rubber molecules in the first series has in the first place a stearic character (rotation solvation), the influence of the temperature on their solvation is relatively insignificant.

This problem has been discussed in detail in work by Staudinger, Fikentscher and Mark,¹⁰ Haller, Whitby, and others.

It was assumed that a lack of any relation between viscosity and temperature, as was observed at the concentrations mentioned above, did not depend so much upon the structure of the solutions as upon the absolute meaning of the viscosity. However the data in Table IV do not confirm such an assumption. This includes the results of measurements of a one per cent rubber solution, the viscosity of which was, by irradiation with a quartz lamp, brought to the value of a 0.1 per cent solution which had not been irradiated. Unlike the latter, the viscosity of the irradiated solution diminished considerably with increase in temperature. The difference in behavior of the rubber which had and which had not been irradiated is particularly evident by a comparison of the viscosities of the irradiated rubber with the viscosities of the unexposed rubber shown in Table III. The rubber solution with a concentration of 0.23 per cent which had not been exposed had absolute viscosity values which were more than three times the values of a one per cent irradiated rubber solution. Nevertheless, this solution did not show viscosity changes corresponding to the temperature.

We are inclined to believe that aggregates of short chains of rubber molecules are present in one per cent irradiated rubber solutions. This would explain their sensitivity toward the temperature effects. In a similar way rubber solutions with a concentration of more than 0.3 per cent which have not been irradiated contain aggregates of long rubber molecular chains. As can be understood, the greater the concentration of the solution the larger are the aggregates of rubber molecules. A study of the surface properties of solutions leads to the conclusion that transformation of rubber into the micellar state is complete at a concentration equal to one per cent.¹¹

The diminution of the viscosity with decrease in the temperature is usually attributed to a process of thermal disaggregation of the micelles in solution. However, Wo. Ostwald¹² was entirely right in calling attention to the fact that disaggregation of colloid particles is manifest by an increase rather than by a diminution of the viscosity. This was confirmed in a striking way by Odens¹³ in experiments with colloidal sulfur. The relative viscosity increased with increase in temperature, and accordingly this phenomenon is accompanied by a parallel increase in the degree of dispersion of the sulfur. The disaggregation of the rubber micelles would have to result in a still greater increase in viscosity, since the molecular chains and the micelles, of smaller circumference due to their configuration, have a relatively higher rotation of solvation. The diminution of the viscosity with temperature of micellar solutions is evidently to be explained in two ways: In the first place, the micellar disaggregation liberates a definite quantity of intramicellar fluid which is

held together by capillary forces. In the second place, an abrupt change in the intensity of the adsorption solvation takes place, since disaggregation of the rubber micelles leads to rupture of the double hydrophilic bonds, and this reduces the quantity of solvent which is combined statically with the rubber.

Furthermore, it should be remembered that at the concentrations mentioned above the relative viscosity of rubber solutions decreases in direct proportion to an increase in temperature. This is obvious from the chart. Consequently the relation between the viscosity and the temperature can be expressed by the equation:

$$\eta_t = \eta_0 - \alpha t$$

where η_t is the viscosity at a given temperature, η_0 the viscosity at temperature 0° and α the constant for the concentration given. Tables I, II, and III give the values

of the relative viscosity calculated by this formula, where the factor η_0 was determined by extrapolation. The values of the constant α increase in proportion to the increase in the concentration of the rubber solution.

The limiting concentration of the solutions in the present work was one per cent. Measurements of solutions at higher concentrations were made difficult by the experimental conditions. The data of Abernethy¹⁴ lead to the conclusion that the linear proportion between the viscosity and the temperature still holds true with solutions containing 10 per cent of rubber. In solutions of higher concentrations, the viscosity and the temperature change according to a certain curvilinear relation. Abernethy's data were obtained with the aid of a ball viscometer. Doubtless the use of a capillary viscometer would have lowered to a smaller limiting concentration the range within which the linear relation between the viscosity and the temperature holds true.

If the range of solutions within which the viscosity diminishes in linear proportion

to an increase in temperature is considered as a region of micellar solutions containing more or less free rubber aggregates, then a more complicated relation between the temperature and the viscosity indicates a more complicated structure of the solutions. In these solutions the rubber micelles are held together and form, as it were, a continuous phase of the system. The influence of the temperature upon solutions of such concentrations is reflected in a disturbance of the union among the individual aggregates and in their disaggregation. The mechanism of such an influence is manifest even in the rapid diminution in viscosity with increase in temperature.

III. Summary

1. The relative viscosity of a rubber solution, the concentration of which does not exceed 0.3 per cent, does not change with change in temperature.

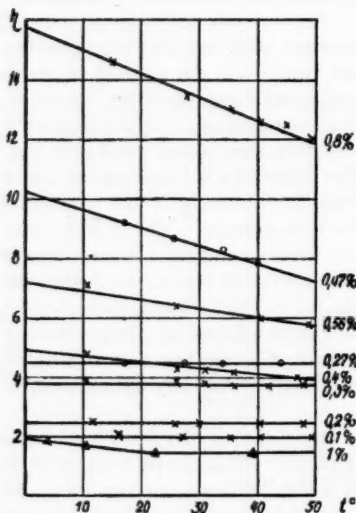


Figure 1

- × Solutions of rubber extracted with acetone
- Solutions of rubber extracted in a carbon dioxide atmosphere
- △ Solutions of unpurified rubber irradiated with ultra-violet light

2. The viscosity of rubber solutions at concentrations from 0.3 to 10 per cent diminishes in direct proportion to an increase in the temperature.

3. Based on the results mentioned above and on the measurements of Abernethy the state of rubber in solutions is characterized by the fact that at concentrations up to 0.3 per cent the solutions are molecular. At concentrations from 0.3 to 10 per cent the solutions contain micelles. In solutions of still higher concentrations the rubber forms a continuous phase of the system.

References

- ¹ Dogadkin and Pantashenkov, *Kautschuk*, **7**, 198 (1931).
- ² *Kolloid-Z.*, **51**, 71 (1930); S. and Leopold, *Ber.*, **63**, 730 (1930).
- ³ *Kolloid-Z.*, **56**, 257 (1931).
- ⁴ *Ind. Rubber J.*, **70**, no. 17 (1930).
- ⁵ *Kolloid-Z.*, **53**, 239 (1930).
- ⁶ See note 4.
- ⁷ *Trans. Royal Soc. Canada*, **23**, 1 (1929).
- ⁸ *Viskosität der Flüssigkeiten* (Russische Ausgabe, page 45).
- ⁹ *Ber.*, **63**, 921 (1930).
- ¹⁰ *Kolloid-Z.*, **49**, 135 (1929).
- ¹¹ By micelle we mean a kinetic unit which consists of a certain number of molecules united by van der Waal's forces. We do not at this time understand the structure of this system.
- ¹² *Grundriss*, 7th Ed., 1913, page 217.
- ¹³ *Z. Physik. Chemie*, **80**, 709 (1912).
- ¹⁴ See note 4.

Diphase Rubber

The Diphase-forming Tendency of Rubber as Shown by the Action of Pigments

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In recent years increasing attention has been paid to a fact emphasized by Weber, *viz.*, that when rubber is carefully treated with solvent two layers separate out, the one drying out to a rubber considerably tougher than the other. The former is the well-known "insoluble" portion, though with exclusion of the protein component it is merely insoluble to a greater degree than the other portion. Its toughness is also to an extent due to the protein it contains.

It has been suggested that rubber is a diphase substance, and also that the harder portion occupies the shell or the skin of the particle. Other very interesting suggestions have been that elasticity is due to the association of the two phases, while recently Whitby has stressed the striking theory that rubber is composed of an unbroken series of polymers.

By the following series of experiments the author has sought to investigate further the suggested diphase property of rubber by an investigation into the separation into "phases" exhibited by the action of pigments. The investigations also produce matter of interest in relation to vulcanization and the behavior of rubber in general.

When rubber is compounded without sulfur and with a suitable pigment such as basic magnesium carbonate, the rubber undergoes a change during the incorporation of the pigment from the soft but plastic and lively condition of the early stage to a dead though still plastic one when higher proportions of the carbonate have been added. It is found, however, on continued addition of the compound that a hardening takes place which is greater than may be expected from its reinforcing effect, especially on consideration of the softening of the rubber from the high mastication and grinding between the particles of compound during the incorporation that it must receive. On continued addition of the pigment to excess, the excessive increase in hardness is quite clear, and it is evident that a change takes place in the rubber, with a considerable reduction in its natural plasticity and tackiness. By treating the magnesium carbonate mix with dilute acetic acid (20%) and sulfuric ether, the soluble pigment carbonate was thereby removed and the rubber isolated. It was found to have changed to a comparatively tough consistency, much resembling vulcanized rubber. On treatment with benzene for some hours, it was only partly soluble, and bore a striking resemblance to vulcanized rubber.

For further investigation of this interesting product, the method was altered to the following:

Instead of incorporating the powders by ordinary compounding on a mill, the rubber was first let down in petroleum ether and benzene, and the powders wetted with benzene were then added. After the mixture had dried to a quite plastic dough it was worked very thoroughly on cold rolls and sheeted out thin while still containing enough solvent to enable it to be moderately plastic. With 3:1 by weight of magnesium carbonate to rubber mix, this amount of solvent was approximately

40% (calculated on the rubber). One hundred grams of rubber were first masticated for four minutes on a laboratory mill. After sheeting and drying at ordinary atmospheric conditions, the mixture was milled a second time on rolls at about 90° F., and sheeted thin. In this milling, strips 10 mm. wide were doubled to a thickness of approximately 2 mm. and sheeted to approximately 0.5 mm., this operation being repeated four times. As the pressure and stress-strain on the rubber between the rolls of a mill involve consideration of the amount and rate of deformation as well as the specific resistance to deformation, the effect of the doubling is obvious. The product was then cut into small pieces, treated with acid as above, then boiled for one hour with acetone—miscible with both benzene and water—to remove the water from the residue, and then treated with boiling benzene. By using acetone to remove the water, drying was expedited and oxidation avoided. Tables show that 78% of this insoluble rubber already referred to was obtained from different samples of magnesium carbonate and, as obtained by the above modified method, was tougher and still more closely comparable with vulcanized rubber.

To distinguish the two components in the remainder of this paper, this insoluble residue will be referred to as "Insoluble A," and the benzene extract will be called "Soluble B." These two substances are found to exist in compounded and acid-extracted rubber in a well-defined manner.

This is shown by the effect of boiling acid-extracted rubber for different periods in benzene (see Table I).

The insoluble residue was washed with solvents after each boiling, and fresh solvent added for the next boiling. The insoluble residue was not allowed to dry in the change-over, so that oxidation would not be caused. The extracts in this case were weighed, and the insoluble was calculated by difference.

TABLE I

Boiling Time	Residue of Insoluble A	Extract
1/2 hr.	79.5 (by difference)	20.5%
2 hrs. additional	76.0 (by difference)	3.5%
5 hrs. additional	72.2 (by difference)	3.8%
17 hrs. additional	67.2 (by difference)	5.0%

The acid-extracted rubber used in this test was that obtained from a mixture of three of magnesium carbonate to one of rubber (by weight). No less than 20.5% is removed in the first half-hour's boiling, and the additional boiling for 24 hours removed only 12.3% of extract, showing that this first 20.5% of extract is not merely produced by degradation through boiling with benzene, but exists already in approximately that amount in the milled compounded rubber as a distinct portion characterized by ready solubility in benzene. Further evidence of the distinction is noticed by exuding the soluble extract into the ether-acid-water extracting solution when ether is used in excess, leaving the "insoluble" distinct and swollen only.

Later experiments on the effect of mastication and different amounts of pigments show that the two "phases" result from the "process" in the presence of the pigments, and there is obviously no evidence of their pre-existence in the raw rubber in the proportions obtained. A further discussion of these components will be made later.

In all subsequent experiments, samples were boiled for two hours, this being considered a satisfactorily distinctive treatment for removal of the readily soluble portion, with a minimum degradation of Insoluble A.

Table II shows the properties of this insoluble rubber compared with vulcanized rubber. The Insoluble A was obtained from a mixing of three parts of magnesium carbonate to one of rubber as before.

TABLE II
COMPARISON OF INSOLUBLE A WITH VULCANIZED AND RAW RUBBER

	Boiled in Benzol 24 Hrs. extract with a jelly- like residue	Residue from Benzene Passed through Mill 150 Times and Boiled Further 2 Hrs. in Benzene Soluble	Permanent Set At Break 30%	Permanent Set At 400% Elonga- tion 30%	Breaking Strain at 65° F., Kgm. per Sq. Cm. 42.2	Volume Expansion in Benzene on Boiling 30 Min. Solution and gel residue	Alteration to Original Shape dur- ing Boiling and after Drying Shapeless gel resi- due
Smoked sheet (Unmasti- cated)							
Smoked sheet (masti- cated)	Almost totally soluble with a jelly- like residue	Soluble	70%	70%	1.1	Solution and gel residue	Soluble
Insol. A ob- tained from 3:1 mag. carb. to rubber mix	10.2% extract	40% extract	16%	16%	42.0	963%	Nil
Vulcanized rubber A	12.9% extract	14.1% extract	9.5%	3%	159.9	690%	Nil
Vulcanized rubber B	9.9% extract	8.1% extract	12.5%	3.1%	172.9	606%	Nil
Vulcanized rubber C	2.8% extract	5.7% extract					

Vulcanized rubber A = 90 rubber plus 10 sulfur vulcanized to 2.8% coefficient.

Vulcanized rubber B = 90 rubber plus 10 sulfur vulcanized to 3.3% coefficient.

Vulcanized rubber C = D.P.G. accelerated sample vulcanized to 2.9% coefficient.

NOTE: (a) Vulcanized samples were first extracted with acetone for 10 hrs. before benzene extraction.
(b) The volume expansion was obtained by weighing before and after the boiling and calculating from the increase in weight.

The results show the definite change the raw rubber has undergone by this pig-menting and milling. The insolubility after milling to such a degree and the simi-larity in the amount of swelling in benzene without losing shape shows this change particularly. The tensile strength tests are not impressive, but it is possible to explain this by the severe treatment the rubber has undergone during the change to Insoluble A; for the rolling and milling—a disrupting action is simultaneous with the actual aggregation; and this disruption may obviously continue after maximum aggregation to Insoluble A has taken place, with a similar effect to the milling of vulcanized rubber. Some consideration can be given to the possibility that Insoluble A is actually a consolidated or cemented network structure, its cellular spaces being due to the removal of pigment particles, and the network itself being the aggregated rubber or Insoluble A which encloses or separates these par-ticles; the cementing or consolidation of this network then being brought about through the aid of the solvents and ordinary cohesion. The main hardness and toughness, of course, is derived from the fibrous condition itself.

On the above considerations, it will be agreed that high tensiles, together with normal permanent set, could hardly be expected from Insoluble A.

Factors in the Formation of Insoluble A

A study of factors in the formation of Insoluble A reveal some interesting facts. Though it appeared that the mineral particles might cause precipitation or coagula-

tion of the rubber, this is not the complete explanation, for it is only after the compounded rubber has been mechanically worked through the mill in the dry state that Insoluble A is formed to any important degree. This is shown by Table III.

TABLE III

	Insoluble A
A. 3:1 Magnesium carbonate to rubber mix, dried only and not sheeted	10.1%
B. 3:1 Magnesium carbonate to rubber mix, sheeted wet, <i>i. e.</i> , while containing approximately 35% solvent (calculated on rubber) and then dried	19.9%
C. Same as B.—Milled and sheeted in dry state after drying out solvent	73.0%

Besides differing so much in amount, *i. e.*, from 10% in the case of A up to 73% in the case of C, the insolubles varied considerably in properties: A, being non-elastic, lifeless, softened by heat, and almost "fibrous," because of its high protein content, and B possessing the elastic and other properties already stated for Insoluble A. It is apparent that the formation of insoluble A in its developed form takes place during the mechanical working of the dry and to a much less extent the partly dry mixing. In A, *i. e.*, the unworked lot, it is at a minimum.

The Effect of Mastication

The degree of mastication of the rubber used has an important bearing on the amount of Insoluble A produced. This is shown by Table IV.

TABLE IV

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Unmasticated	100 G. 4 Min. on Lab. Mill	10 Kg. on 54" Mill for 20 Min.	10 Kg. on 54" Mill for 40 Min.	10 Kg. on 54" Mill for 80 Min.	10 Kg. on 54" Mill for 110 Min.	100 G. of No. 6 Ground 15 Min. on Lab. Mill
Insol. A 77.5%	71.1%	66%	61.4%	57%	51.5%	27.5%

(No. 7 masticated rubber was very plastic, adhering to the mill surface at even 80° F.)

From this it may be said that the amount of Insoluble A obtainable varies inversely with the mastication of the rubber; and if mastication itself could be stated in definite terms, a certain ratio would presumably be found. Conversely, it is apparent that mastication can be stated with reference to the Insoluble A chart, *i. e.*, in inverse terms of Insoluble A.

Effect of Proteins

Though it appeared probable that the protein components might be closely connected with the formation of Insoluble, this was found not to be the case by re-compounding with 3.1 magnesium carbonate in the previously described manner a soluble B obtained from extraction with petroleum ether. (Benzene was replaced with ether so that degradation would be minimized.) The amount of Insoluble A obtained was 59%.

The removal of resins, etc., by acetone-extraction had an effect similar to the removal of proteins, causing a reduction in the amount of Insoluble A.

This reduction of Insoluble A on the removal of both proteins and resin could have been at least partly due to the extra total degradation accompanying the extra treatment.

Further investigation into this matter of the proteins was made by separating ordinary smoked sheet into its two ordinary components by standing in benzene. The "ordinary" so-called "insoluble" obtained on the separation was 45%, and the

"soluble" 55% of the total original rubber. These respective rubbers obtained—the "soluble" and the "insoluble"—were treated for Insoluble A with magnesium carbonate in the usual proportion of three to one by weight. The amount of Insoluble A thus obtained was only 4% less from the "soluble" than from the "insoluble" portion, but was of a softer character. This is of interest and importance, and will be considered later.

Different rubbers, smoked sheet, Para, *ficus elastica*, and different samples of pale crepe, as expected, did not coincide in the amount of Insoluble A obtained. It is interesting to note that *ficus elastica*, the latex globules of which have been shown by Hauser to have a soft shell in comparison with Heveas, yielded an amount of Insoluble A within a few per cent of the lowest pale crepe sample, but a product of a softer nature. Thus, the effect of an outer shell on the yield of Insoluble A can be gaged, and the change in the rubber to Insoluble A cannot be attributed merely to such a shell.

Effect of Different Compounds

Different compounds produce an outstanding difference in results. This is shown by Table V, which shows the maximum amount of Insoluble A obtained with different compounds. It will be seen in the case of sulfur that the amount of Insoluble A is practically nil, while with light magnesium oxide up to 84% is obtained.

TABLE V

	Zinc Oxide Ordinary	Magnesium Carb. 1	Magnesium Carb. 2	Magnesium Oxide	Zinc Carbonate	Lead Oxide	Sulfur	Dextrine	Sodium Borate
Insol. A.	82%	78.3%	68%	84%	47.2%	32%	2%	Nil %	40%

The sample of magnesium carbonate No. 2 giving the lower percentage of insoluble was a heavier sample than No. 1. The zinc oxide "ordinary" was a lead-free quality, and produced by a modified condensation method, and was before mixing of unusually large particle size, many of the particles being well-defined prism and twin and trilling crystals. In the case of all compounds, direct treatment with benzene, *i. e.*, without first removing the mineral compound by acid treatment, was practically valueless, owing to the varying permeability of the different mixtures, particularly in the higher proportions of pigment compound.

Effect of Different Proportions of Compounds

A most interesting and important feature is presented in the effect of varying amounts of the different compounding materials, and Chart 1 shows the effect of magnesium carbonate, zinc carbonate, zinc oxide, both ordinary and "Kadox," sulfur and magnesium oxide in varying proportions. It will be seen the graphs of Insoluble A to pigment take the form of well-defined curves. There is, therefore, a certain proportion of each compound to rubber, that gives maximum amount of Insoluble A, and an increase on this amount of pigment compound causes a reduction in the amount of Insoluble A formed, the rate of this reduction varying with the pigment and the amount of the maximum quantity formed. Of particular note is the long plateau but high optimum in the case of ordinary zinc oxide; the steep and high curves of black seal "Kadox" zinc oxide, magnesium oxide, and magnesium carbonate. The curve of zinc carbonate is of much lower dimensions, while Insoluble A curve from sulfur is almost non-existent, and this appears of more than usual interest. It was found, however, that, even on replacement of the benzene with petroleum ether in the process of mixing, recrystallization of the

sulfur to larger crystals took place. Combined with this property of sulfur is the low melting point and comparative flexibility of the particles. As to whether the sulfur possesses some other special property is, therefore, rendered doubtful, but the affinity for rubber, as shown by its solubility in it, might well indicate another effect.

Experiment with Dextrine

The effect of pigments, such as carbon black and clays, could not be compared with that of the compounds shown by the foregoing method. A modification of the method to overcome the impermeability to benzene of the high compound mixtures gave satisfactory results. In this method extraction with acetic acid was dispensed with. It was thought that by incorporating a substance that could then be removed by a solvent without effect on the compounds or the rubber, the impermeability

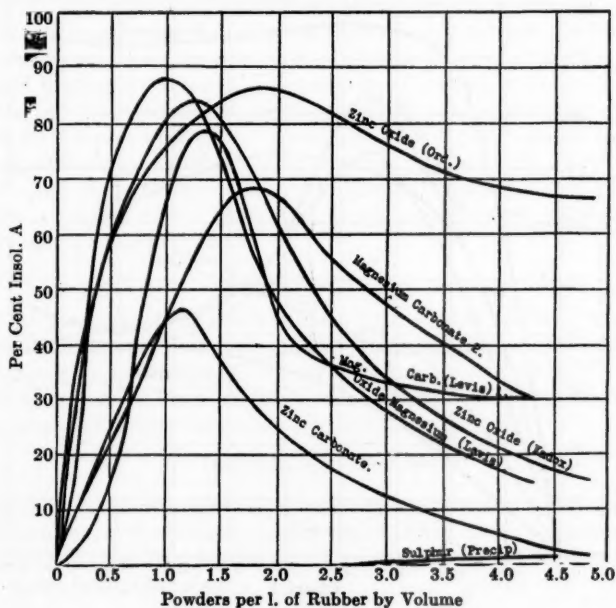


Chart 1

to benzene of the hard sheeted mixings could thus be overcome. The substance chosen was dextrine, which is of large particle size and definite shape, and readily soluble in water, and has little, if any, Insoluble A-forming properties. (Proportions of four of dextrine to one of rubber yielded no Insoluble A whatever.) It was used in these experiments in equal proportions to the rubber itself, and the varying amount of compounds added in addition. The removal of the dextrine—by treatment for some hours at 130° with water—was calculated to leave a microporosity, and thus increase the total surface exposed to the benzene. This worked satisfactorily except for minor difficulties, and the results, shown on Chart 2, give the essential features that the previous method did with the compounds, such as magnesium carbonate and zinc oxide, that can be treated by both methods.

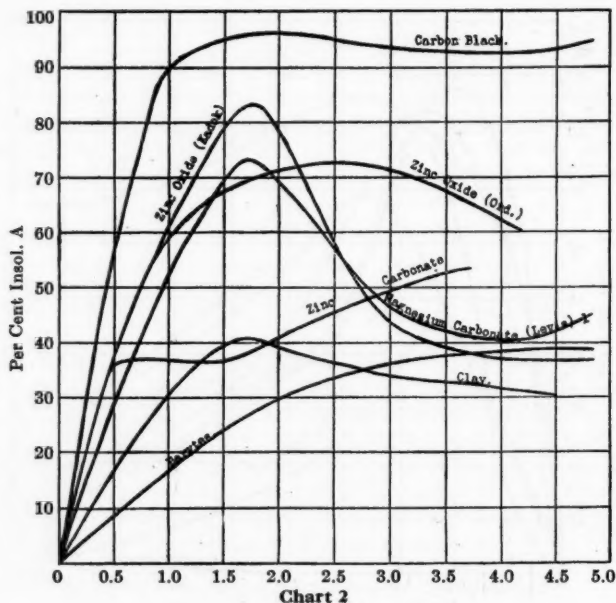
The principal difference in the curves, as would be expected, is that the height is reduced, i. e., the maximum amount of Insoluble A is reduced, and the highest point

corresponds to a higher percentage of compounds. The zinc carbonate has acted in a perverse manner. The insoluble compounds show interesting results. Altogether, the curves obtained are of striking interest.

Effect of Different Substances

Diphenylguanidine, with magnesium carbonate as pigment reduced the amount of Insoluble A, while "A-19" increased it a little. Oils and softeners, as would be expected, also reduced the amount obtained.

Antioxidants, such as "Oxynone," "Neozone," and pyrogallol, increased the amount of Insoluble A, and increased its toughness considerably. However, when hydrochloric acid was used instead of acetic acid to remove the pigment this increase was not manifest, and the increase with acetic acid was apparently due to



oxygen, or to oxidized products of these oxidizable substances. This action is, in fact, obvious from the entire blackening of the Insoluble A product by the use of these substances and acetic acid; a significant effect in general, seeming to indicate the physical attachment of this oxidized product; the effect resembling dyeing.

Retreatment of the Insoluble A with acetic acid, etc. (after complete isolation and drying-out), caused further degradation, so that up to 13% of extract was obtained after such retreatment.

This additional soluble obtained is probably due to oxidation during drying, etc., for prolonged treatment of a lot with the acid mixture for 10 days instead of the normal amount of three days, had practically no additional effect on the three-day result.

This prolonged treatment with acid also removes doubt as to the importance of acetic acid in the production of Insoluble A.

It is interesting to note that treatment of unmasticated smoke sheet with acetic acid and extraction with benzene produced 25% to 35% of a very indefinitely defined insoluble, which was plastic and shapeless; while similar treatment of smoked sheet masticated to the same extent as that used in the pigment experiments produced a certain amount of gel fraction which could not be separated and estimated. Treatment of ordinary smoked sheet with benzene for two hours yielded a percentage of soft and inelastic residue nearly similar to the smoked sheet treated with acid. Sodium borate crushed to approximately 1.6 mm. produced 40% Insoluble A. In this case the extraction was done with water only. Thus, it is evident that while acetic acid, or resulting nascent gases may have some small effect on the amount of Insoluble A obtained, it is by no means essential for its production.

Effect of Heat

The effect of heating the 3.1 magnesium carbonate mixture for 15 minutes at 285° F. was to cause a reduction of 10% in the amount of Insoluble A obtained. The effect of heating the Insoluble A itself out of contact with air, was to slowly increase its solubility, and amounts varying from 5% to 15% of extract were obtained on heating 60 minutes at 280° F. Heating in air rapidly caused oxidation and degradation, up to 75% of extract being obtained by heating 60 minutes at 280° F. The use of a high temperature on the mills during the rolling and working causes a considerable reduction in the amount of Insoluble A formed, particularly in the mixings of highest rubber content.

Effect of Pressure

Using a 3.1 magnesium carbonate mixing, a direct and relatively static pressure of 250 tons to the square inch between the plates of a press produced 48% of Insoluble A, against a maximum of 78% when rolled through the mill. Apparently, research of these lines by the use of more static pressure will be of value, and enable tests to be made that appear in doubt by rolling through a mill.

Impurities in Benzene

The purity of the benzene was important, and the addition of certain substances, such as turpentine, to the benzene to the extent of 2%, had a pronounced effect on both the production and the condition of the Insoluble A, the accelerated degradation of the latter being obvious.

General

It was found that a small percentage of ash, from 1% to 3%, is very difficult to remove from the Insoluble A residue. This appeared to be in some kind of combination with the non-rubber components, and did not seem of important significance in regard to the insolubility of the Insoluble A product.

Some Aspects of Insoluble A and Its Formation

It will be seen that the Insoluble A of these experiments is not a definite unvarying substance of definite physical properties. In fact, the relative amounts of Insoluble A obtained are, to a degree, also indicative of the physical properties of the product, and with the increase in the amount of Insoluble A there is an increase in its insolubility. For one rubber and one pigment there is a difficultly defined relation between the physical qualities of hardness, elasticity, etc., of the Insoluble A, and the amount of it prepared under standard conditions with the different amounts of the pigment. This ratio becomes more variable under certain influences,

and alterations in the method of treatment has this effect. When a 3:1 magnesium carbonate-rubber mix was passed through the mill rolls 100 times in addition to the ordinary number required to produce the change to maximum insolubility, it showed a reduction of only 10% in the amount of Insoluble A obtained, but the product was physically changed completely, and dried out to a shapeless mass. Again, the ratio varies with the pigment, and the Insoluble A from the light basic magnesium oxide had comparatively low physical properties, and, though the amount obtained was as high as 84%, the physical properties were noticeably inferior to those of the zinc oxide and magnesium carbonate products. Why there should thus be a difference has, no doubt, an important explanation, and in the case of the shapeless residue obtained by the increased working, it is obviously of interest to question if this is due to the breaking down of the particles and the general weakening of the bonds of attraction, or whether the mass holds together by certain residual or secondary bonds, while other bonds have been destroyed. Incidentally, the results have a bearing on the effect of solvents generally, and the relation of solvent effect to the state of "cure" of vulcanized rubber. Besides the variations in the relation of physical properties to the amount of Insoluble A, variations in the relative amounts of Soluble B and Insoluble A formed readily occur, and reasonably good duplicates are obtained only by closely repeating the conditions of production. This is what might readily be expected from an analysis of the various factors and influences in its formation.

The Two Phases

Of particular interest is the apparent formation of two phases—that is, the separation of the rubber into two distinct solubility fractions. As indicated by the varying amount of Insoluble A obtained with different proportions of pigments, as well as by the decrease in quantity obtained after a certain maximum, it is evident these "phases" do not pre-exist as fractions in the rubber, and it appears that the relative amounts of Soluble and Insoluble A are formed by certain rules of equilibrium with the introduction of the pigments and the application of pressure stress-strain. Nevertheless, there was reason to contend there is a degree of arbitrariness in the determination of these two rubbers with benzene being as the determining factor. This is emphasized in the light of Whitby's paper,¹ in which he has drawn attention to the fact pointed out by Gladstone and Hibbert,² that the so-called insoluble in raw rubber is variable according to the solvent used. The action of different solvents on the entire rubber product of the pigment action over various periods of boiling is of much interest. Three solvents were used in addition to the benzene, *viz.*, toluene, petroleum ether (range around 38° C.), and ethylether. The results are shown on Chart 3. The curves produced by petroleum ether and ethyl ether are similar in type to those of benzene, with the exception that the amount of the readily soluble portion is less. The toluene curve is also essentially the same showing the same separation into the readily soluble portion—in this case, much larger in amount—and the more difficultly soluble one.

In the case of toluene, it is obvious the disintegrating or degrading effect is relatively much more severe than with benzene or ether. It is evident that beside the difference in affinity of the particular solvent molecules and the increased kinetic energy of the higher temperature of this higher boiling point solvent, there is the effect of the increased heat on the rubber itself; and the general effect is, therefore, a multiple one, and certain temperatures will be reached above the range of true comparison. In agreement with this the Insoluble A, even after treatment with benzene for 24 hours, was very little altered in hardness and toughness, in fact,

the residue from petroleum ether after 24 hours was distinctly drier and harder. That from toluene, even after the first half-hour's boiling, was considerably tackier, and, while the Insoluble A itself shows the effects of this extra action of the toluene by quicker disintegration, any increased effect is obviously not readily seen with Soluble B, and the relative effect on the Soluble B and Insoluble A is consequently not portrayed.

The relationship of "ready solubility" to comparative "insolubility" can therefore be considered reasonably well maintained throughout a variety of solvents. Nevertheless the variation that does exist in the relative amounts of Soluble B and Insoluble A obtained from different solvents seems to be significant, notwithstanding the curve similarity, and requires some explanation.

The step from the soluble to the insoluble is not an abrupt one, as would be expected.

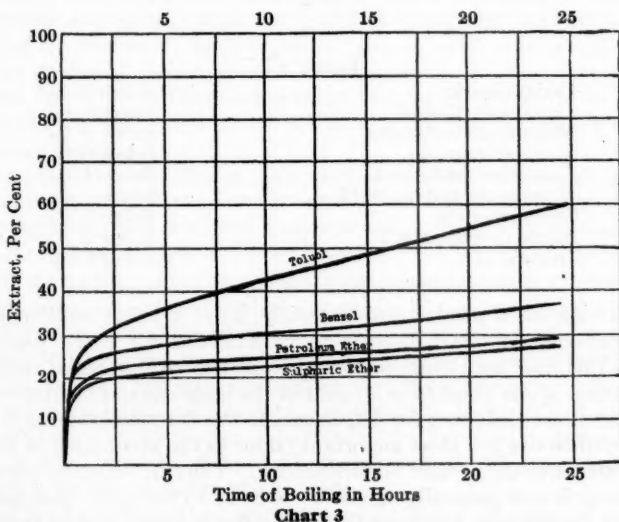


Chart 3

Further, Chart 3 shows that it is theoretically possible to obtain a solvent from which the amount of solvation or Soluble B would approach nil, but such resistance to solvation would obviously become all the more definitely a function of temperature.

It might be still contended that after action by pigments the rubber is composed of units in regularly ascending scale or gradient, and that the apparent difference in the two separated products is merely due to a critical point in the solvating properties of the solvent. Thus in the case of any one solvent, ready solvation takes place up to a certain grade of polymer or aggregate, and then—sharply—virtually ceases. This is very unlikely, but the existence of two phases, *i. e.*, two rubbers with a distinct contrast in properties, together with certain critical properties in solvent effect, for example, boiling point, is more reconcilable. Boiling in ether for two hours would thus remove the greater part of the soluble, that is, the portion of the rubber that has been left unacted on by pigments; and the solvent effect would extend into the Insoluble A, that is, the more acted-on or transformed rubber, while toluene will remove practically all this "soluble," and move further upon the Insoluble A. At a certain point beyond the boiling of 24

hours the Insoluble A would probably disintegrate rapidly, producing a fall in the curve produced. This, however, was not confirmed, 24 hours being the longest period used.

A study of the effects of different temperatures with the one solvent no doubt would be of much value, and it seems likely a further examination of the relationship of the two fractions, Insoluble A and Soluble B, would be of considerable interest and importance. Meanwhile, the investigation into the fractions can be continued with increased interest.

Relation of Insoluble A to Size and Other Properties of the Particles

Comparison of the particle size of the various compounds mentioned with the Insoluble A formation shows a significant relationship between the two. The results of the determination of the particle sizes of the compounds used are shown in Table VI.

TABLE VI

Carbon black	Below 0.5 μ
Zinc oxide (Kadox)	Below 0.6 μ
Magnesium carbonate	Below 0.9 μ
Magnesium oxide	Below 0.6 μ
Zinc oxide (ordinary)	Below 1.0 μ
Magnesium carbonate (2)	Below 1.2 μ
Zinc carbonate	Below 1.6 μ
Sulfur (precipitated)	Below 1.0 μ
Dextrin	Below 7.0 μ

The determination of particle size, generally, is not yet very satisfactory, and no entirely satisfactory method appears to be available for every pigment. The particles in this case were examined on the finished and prepared mixing, owing to the reduction in size possible as a result of the large amount of friction produced in the preparation. Allowing for deficiencies in the determination, it is quite evident that particle size is a most important factor in the production of Insoluble A. But there are obviously other considerations. Thus in ordinary compounding, specific surface is now generally agreed to be more to the point than particle size, and particles, for example, which are lamellar or flat in shape, possess greater specific surface than do those of the cubical type with similar cross-section under the microscope. The nature of the surface also will affect the specific surface or surface area, and no doubt a considerable difference exists between certain different compounds in this respect. Part of the surface of each barytes particle, for example, will be irregular, and expose various irregular projections, or the corners of small rhomboid crystals. In the case of infusorial earth, the particle size is not a true indication of the surface, owing to the peculiar nature of the structure of the diatoms. Certain types of carbon black existing in a mix are no doubt examples where the particle size may not be a very close guide to the specific surface.

As well as being important in ordinary compounding, specific surface can be expected to be of importance in Insoluble A formation. In addition to size, there is the question of shape. As the compression and stress that can be applied depends on the thickness of the film between the particles, *i. e.*, the rigidity of the mix, and as compression is essential for the Insoluble A formation, anything affecting this thickness must be taken into account. If, for example, two kinds of particles be considered of different shape—the one cubical, the other spherical, and both of similar size—those of the cube shape could be “packed” in the rubber, so that there is an equal thickness of rubber between every two opposite faces, with a small in-

crease at the opposite corner and edges; but in the case of the spheres the position is entirely different, and the rubber between the particles must vary considerably in thickness.

The difference in the difficulty of packing, and particularly in irregularity of size, will also vary the effect, for if the cubical particles consist of, say, two diverse sizes, the film between the particles must necessarily vary considerably in thickness owing to the prevention by the smaller particles of the larger particles meeting in order. As perfect regularity, in any case, is only likely to be theoretically obtainable in a pigment, it can be assumed that the pigment with the greatest Insoluble A-forming effect from the standpoint of size, assuming everything else to be equal and the average size to be equal, will consist of the most efficient blending of sizes and shapes, so that the smaller sizes may pack the spaces between the larger particles, and the old shapes satisfactorily interlock and interpose. Certain "lines of force," no doubt, exist between the particles of pigment, and these will effect the placing of the particles. In short, these various factors may be said to compose the "packing qualities" of the pigment. For the reason of the necessity of pressure, etc., to form Insoluble A, the melting point and hardness need to be considered, and substances like sulfur and starch will have a slower effect, owing to their low figures in these respects.

Of further interest is the affinity of the particle for other substances, as shown by the comparatively recent and very interesting results obtained by investigators concerning the adsorption of different gases on the surface of carbon black particles. It would be possible for these adsorbed gases to have a two-fold effect in rubber, in that they may partly satisfy the affinity of the carbon black or other particles, reducing the effect of certain possible attractions of the particles for the rubber; and, secondly, that they themselves might directly affect the rubber and its proteins, resins, and complex components. In the present experiments, however, during rolling through the mill, these gases should be removed; but, again, this likelihood would vary with the pigment, and would be more difficult to effect with carbon black than with the coarser and differently constructed particles.

Finally, in this formation of Insoluble A there are electro- or physico-chemical forces, to which further reference will be made.

From this brief summary it is, no doubt, essential that the term of average fineness in the formation of Insoluble A has to be used with reservation. This property of a pigment to cause insoluble formation should be more suitably referred to as the "*Insoluble A-forming value*." This figure, incidentally, should be one of considerable usefulness in classifying the properties of a pigment. Obviously, fineness or specific surface must be the prime factor, and must serve as the basis for investigation into the phenomena of Insoluble A formation.

It is interesting and necessary to discriminate between fineness as itself responsible for the change in the rubber, and the fineness as evidence of the existence of other forces existing in a degree—for each pigment—corresponding to the fineness.

The Study of the Fall in the Insoluble A

The curves shown on Charts 1 and 2 are obviously of much interest and importance, and the fall in the Insoluble A after a certain maximum is particularly interesting. Clearly this can be considered, at least, partly due to mechanical causes. Thus increased plasticization might be expected from increased grinding of the rubber following an increase in the percentage of particles of pigment. This, however, is not of fundamental importance as the milling of a mixture of 10:1 magnesium carbonate to rubber, to the extent of 1000% above that required for the formation of

maximum Insoluble A, caused an actual increase in the amount of Insoluble A obtained, viz., from 40% to 49%; while a 3:1 mixture showed a reduction of only 10% on similar working—from 78% to 68%. As already mentioned, the physical qualities of the latter were much affected, however.

Then there is the increasing of the area of rubber exposed to the solvent on the removal by acid of the increasing percentages of pigments, which should be expected to cause increased solvation. While the curves of the finer pigments, Kadox zinc oxide and magnesium oxide, might appear to support this as a major cause—for the finer the pigment the greater the surface exposed—ordinary zinc oxide, as against magnesium carbonate, which particles are of similar size, does not do so.

Another explanation entering more into the truly physical force aspect is that of "obstruction." If Insoluble A is regarded as an aggregation of particles or molecules, then aggregation will take place at certain bonds of attraction. The effect of increasing pigments will be, therefore, to cause a larger number of bonds to lie unattached, or attached in a negative way, against the pigment faces. But the curves of carbon black and zinc oxide and magnesium carbonate again show that still more is required as an explanation.

If, on another assumption—that the effect of the insolubility is due to an adhesion of the rubber particles to the pigment surface (an adsorption), then in such case the removal of pigments will release the rubber particles to the solvent attack. This might not disagree with the insolubility in the mixing containing carbon black, which, of course, cannot be removed, but does not fit in with the Kadox zinc oxide or magnesium oxide curves, for in these cases maximum Insoluble A of high insolubility is obtained on the removal of the pigments, and the amount of insoluble obtained by the dextrin experiment, in which the pigments are not removed, is certainly not more than when they are removed—to a defined point—and is, in fact, even less. This actual decrease is however apparently due to the small addition of practically neutral dextrin surface.

The results with zinc carbonate require special consideration, and these appear at first sight to support to some extent this last-mentioned view—point of adhesion—for by the acid pigment extraction process the insoluble is reduced to zero, while with the dextrin process it actually increases. This effect might have some explanation in the low aggregating intensity or low specific surface of zinc carbonate, in so far that the solvation would increase with the increase in area exposed to solvents accompanying the removal of the increasing proportions of pigment, and this, together with the action of "obstruction," would successfully counteract the low specific insoluble-forming capacity of the zinc carbonate, this latter, however, actually continuing to function, as shown by the dextrin experiment curve. This would not preclude a fall in the insoluble ultimately—but at too high a proportion of zinc carbonate pigment to be handled successfully. The zinc carbonate would actually, therefore, in such a case have some essential resemblance to ordinary zinc oxide. Some distinction, however, may be made in explaining this rise in the dextrin-zinc carbonate curve in the general conception of *impermeability*, in which the tendency of the pigment particles to cohere, with the consequent difficulty of extracting the enclosed rubbers of varying viscosity, is also taken into consideration. It will, of course, be noted that as the zinc carbonate pigment increases, its ratio to dextrin—the agent for permeation of solvent—must necessarily increase also. The dextrin could not be increased further to compensate for this increase without mechanical complications in the working on the mills, etc.

It is of interest to note, apropos to these suggestions, that zinc carbonate, itself in pigment form, compresses to a distinctly harder condition between the rolls of

a mill than any other of the pigments. Reverting to the pigments, Kadox zinc oxide, magnesium carbonate, etc.—these also show a certain impermeability, *i. e.*, and increase in insolubility, as shown at a certain point in the "Dextrin" curves, but in each case this increase is less than that with zinc carbonate—and this in the face of their higher insoluble-forming properties with, at the same time, their greater drop in the curves before this "recovery" takes place. This indicates that the actual formation of Insoluble A is not the only factor responsible for the impermeability, even allowing that a reversal in some form of charge had taken place at these points, phenomena so notable in colloidal action. It is evident in all, that though, no doubt, an adhesion or adsorption of the rubber can, and does, take place with various pigments, this actual attraction is not necessarily the cause of insolubility, even though maybe this attraction was an important factor in the change to insolubility in the rubber.

It was also clear that notwithstanding the undoubted importance of the foregoing mechanical and purely physical effects, another factor was required to complete an explanation of the various drops in Insoluble A, and it was apparent the elusive and difficultly identified electro properties of the pigment, which have been at various times referred to by investigators, would be a likely field for investigation.

The Electrostatic Effect

The curves themselves actually bear a striking resemblance to those of albumen in solution treated with varying amounts of electrolyte, this effect being usually attributed to a reversal of charge with precipitation taking place near the isoelectric point. A similar effect is that of the multivalent ions, such as trivalent aluminium on gold sols.

Unfortunately, the study of rubber as a colloid has not received the benefit of the very considerable and important work done on colloids generally. The results of the characteristic researches in velocity, mobility, osmosis, etc., done with a dispersion medium, water, have not been correlated with the behavior of rubber in the dry state, in which state practically its whole value to date has rested.

It is of peculiar interest that the type of Insoluble A curve produced by the different pigments bears some relationship to the electrostatic charge obtainable from these pigments alone.

Table VII shows that ordinary zinc oxide, which produced the curve of long plateau, is the only negatively charged one of the group, carbon black, of course, being a moderate "conductor."

TABLE VII

Pigment Compound	Charge Exhibited with Excitants		
	Paper	Porcelain Mortar	Steel Mill Rolls
Kadox zinc oxide	Positive	Positive	Positive
Ordinary zinc oxide	Negative	Negative	Negative
Magnesium carbonate	Positive	Positive	Positive
Zinc carbonate	Faintly positive	Faintly positive	Faintly positive
Magnesium oxide	Positive	Positive	Positive
Carbon black
Rubber	Negative	Negative	Negative

The completely different electrostatic properties of Kadox and ordinary zinc oxide are more clearly shown in the following table:

Zinc oxide (ordinary) to rubber or ebonite	= Negative charge
Rubber to porcelain mortar	= Negative charge
Mortar to brown paper	= Negative charge
Paper to steel	= Negative charge
Steel to Kadox zinc oxide	= Negative charge

(Where necessary the pigment was first highly compressed between the mill rolls.)

The exact nature and cause of electrostatic charges is still somewhat indifferently explained. Clearly, however, the charge manifested by the electroscope does not denote the same definite corresponding property, but is merely that of the relation of one substance to another. Even so, in this respect there is something in common with the electro-behavior of substances in the dispersion medium, for the charge is relative in this case also and varies with the medium, so that, for instance, glass, which is "positive" in water, is yet "negative" in turpentine. The task of determining any connection between the reversal of Insoluble A formation in the mixes themselves and the electrostatic behavior is obviously a very difficult one, owing to the induced charges and the undeterminable specific friction of the components of the mix, as in the mix. It should provide a very interesting series of experiments, however.

While the electrostatic charge produced by the passing of pigment particle over rubber particle, or both, against a common excitant, need not be considered at this juncture in itself the cause of the change in the reduction of Insoluble A, the difference in charge undoubtedly denotes some difference in the electronic condition of the pigment particle, and this difference could reasonably be expected to have an important contribution to the causes of the drop in Insoluble A.

To further study the effects, the upward movement of the curve requires consideration.

Increase in Production of Insoluble A

In the production of Insoluble A, several facts are of importance:

1. Mastication of the rubber causes a reduction in Insoluble A.
2. The toughness and insolubility of the product increases with the amount obtained.
3. Pressure, and probably stress-strain, is necessary to cause the change.
4. There is a maximum obtainable from each pigment and this varies with the pigment.

1. *Mastication.*—It appears likely that one effect of mastication on rubber may be that of an activation of the particles of the rubber with an electronic rearrangement, or the creation of more surface by the reduction in size of the particles, primarily by the direct effect of the heat of mastication, with the mechanical action.

Oxygen of the air has been demonstrated by Grenquist,³ and again by Cotton,⁴ to have a very important effect, and this action could be caused by assisting the above increase in surface by the attaching of the oxygen to the surface of the particles formed, thus affecting their cohesion and reunion. More inert gases might be expected to have this effect also to some degree. Though, as Cotton⁴ has shown, plasticization of the rubber is at a low rate when out of contact with the oxygen of the air, and air that is minus oxygen might, therefore, appear the indispensable factor, it is, nevertheless, a fact that ordinary rubber will withstand the effect of oxygen (in the dark) for a very long time. The author has submitted a thin sheet of raw rubber to treatment in an oxygen bomb at 152° F. and a pressure of 300 lb. to the square inch for 50 hours without any apparent degradation; thus proving that the mechanical rupture of the rubber in mastication is also an essential.

Oxygen has sometimes been considered as having one action on rubber, *viz.*, causing tackiness and breakdown, but its action when antioxidants, such as "Oxynone," are present, or peroxides, as shown by Ostromislenski, shows a rather different effect, *viz.*, that of a hardening or a kind of vulcanization.

Assuming the possibility of such an effect in mastication, providing the necessary substances be present, there will be this tendency to toughening or hardening, but,

simultaneously, as a result of such toughening, a greater adsorption of mechanical energy and thus more drastic ultimate degradation. This latter is exemplified in the use of Oxynone or a few per cent of basic magnesium carbonate for in such cases a pronounced stiffening of the rubber takes place at the outset of mastication, followed by greater plasticity than if this stiffening had not taken place.

The presence of copper, on the other hand, leaves no doubt as to the different effect of oxygen. It shows no preliminary stage of aggregation, but has the one action of degradation—the rubber is completely broken down with an entire alteration to its "nature" or intrinsic properties, and is changed to an oxidized product.

Thus, the effect of oxygen added as a result of exposure to air during mastication could possibly be a complicated one.

Another possible effect of mastication which is rather debatable is that indicated by the loss of energy during stretching of rubber, an action that is continuous during the masticating process, but which is of course reversible to a degree.

That some change takes place in the rubber has been well demonstrated by x-ray diffraction patterns and the liberation of heat, and again by the remarkable experiment of Feuchter⁵ in the racking of rubber. It is doubtful if the effect is entirely reversible on the release of the strain, and the continued rupture of the resulting rubber is evident. The outcome of the action, and in fact that of the former action of oxygen can be illustrated in extreme by crushed vulcanized rubber, this vulcanized "crumb" possessing low cohesion, and the mass of crumbs being of very considerable mobility and low tenacity, even after making due allowance for the adsorbed air layer. The remarkable depreciation in strength of rubber, first definitely converted to Insoluble A and then compounded, is shown under "manufacturing effects." While this latter, admittedly, is an "affair of the pigments," it nevertheless serves to further illustrate the bonding or unifying of units and the fracture of the product at other bonds. As confirmed by the researches of Grenquist, plasticization of rubber in the cold is most severe. This condition is best obtained by using a thin layer of rubber around the mill rolls. And though, no doubt, this effect is partly due to the increased rigidity or resistance of the cooled rubber, and thus greater absorption of mechanical energy as well as to increased exposure to the air and oxygen, the above effect of orientation or coadunation from stretching seems to have to be reckoned with. Maybe it is during the subsequent rupture that some oxygen finds anchorage in the rubber.

In agreement with the views of previous authors it certainly seems necessary when considering mastication to differentiate between disaggregation and degradation or comminution.

The former action is, perhaps, best represented by the effect of heat when the aggregates should be, in a sense, merely "resolved." The resulting particles would be not incapable of reuniting in the original order when the rubber remains undisturbed. (And yet showing, as it does, the variety of the problem, it is to be expected that during this additional heat oxygen will show the greater chemical action.) In the case of comminution, on the other hand, the aggregates or assemblies may be broken by sheer force, and will be prone to fracture at different linkages or across different planes. In fact, as seen by possible orientation and polymerization with oxygen compounds new bonds may be formed, and the resulting product of the mastication still further removed from the original type through the destruction of this product.

The amount of "recovery" on standing should indicate the true disaggregation, but, even in this, the recovery could be partly due to the "residual or unaffected power to aggregate."

Mastication is unquestionably one of rubber's most interesting problems, and surely involves consideration of its essential properties, *i. e.*, its molecular structure and arrangement.

The failure of the pigments to produce the same amount of Insoluble A with highly masticated rubber as with ordinary rubber could, therefore, be partly due to the failure to neutralize the temporarily increased energy of repulsion of the system, as, for example, that from the action of heat, and partly to the permanent reduction in the power of attraction of the units of the system. Clearly, however, the above effect of the pigments demonstrates that the maximum aggregation effect is dependent on the particles existing in their original condition and configuration, a fact of appreciable significance.

2. *Increase in Hardness, etc.*—Of particular interest is the fact that the degree of aggregation, *i. e.*, the hardness and insolubility of the Insoluble A product, increases as the quantity formed increases (though apparently not in a simple ratio), so that when the aggregating agent is increased, *i. e.*, the proportion of pigments, instead of the rubber become all transformed to an average degree, this fraction called Insoluble A not only increases in quantity but increases in its hardness and insoluble characteristics, with the reduction in quantity of the Soluble B, and the distinction between the two components becomes all the more clearly defined. This fact would make adsorption inadequate in itself as an explanation of this action of pigments. It could be viewed that Insoluble A formation takes place according to the original polymers in the raw rubber, and that the progressive effect of the pigments is a progressive action on the graded polymers. This explanation, in any case, is obviously incomplete in itself, as shown by the fact that when a certain ratio of pigment to rubber is exceeded the Soluble B increases. At most, it is obvious that to explain the action thus is but to transfer the essential part of the problem to that of the existence of the polymers themselves.

The two-phase condition of ordinary rubber becomes more important in view of this increase in the insolubility, and helps to throw light on the action. Inasmuch, as previously remarked, these phases are somewhat indistinct in that they are variable to the solvent used, there is a resemblance to the product obtained from low percentages of pigment in which the distinction between the so-called soluble and insoluble is also small. The importance of the non-rubber content of raw rubber has long been recognized in its effect on vulcanization, but it was apparently natural for it to possess as well certain other effects than merely a catalyst for vulcanization. "It is rather too much to hope that nature had been so considerably disposed to the automobile and rubber industry generally!"

It is, therefore, of interest that Rhodes and Bishop in their researches have shown that lipins produce the remarkable effect of converting raw rubber on a mill to a somewhat brittle state, an effect reversible on continued working.

It has been shown in these experiments that antioxidants like Oxynone increase the insoluble in certain circumstances, and they are also known to increase insolubility of rubber under the action of light. An antioxidant such as Oxynone, as is well known, causes a hardening when first added to the pure rubber in an ordinary mixing operation. The non-rubber components are notably complex in character, but the known existence of Lipins and oxidases connects them to these actions. It seems a reasonable assumption that certain at least of the forces involved in the formation of a relatively insoluble fraction in raw rubber are related to those of the action of pigments.

It will be recalled that raw rubber from which the non-rubber components insoluble in benzene had been removed yielded an almost similar amount of Insoluble

A when acted on by pigments, as did a portion high in these components. It will be realized, of course, and due allowance made for the fact, that the hardest and most aggregated portion would thereby be liable to mechanical disruption during incorporation of the powders, and so this would be responsible for some reduction in Insoluble A.

Another lot with resins removed also produced Insoluble A. It was an obvious query as to whether this diphasic condition is an adjunct to the presence of these foreign substances in the form of the non-rubber components, pigments, etc., *i. e.*, that separation into phases is dependent on the presence of these substances, or whether a similar syneresis can take place by some thermodynamical or crystallization operation as well.

Dealing again with this effect of the pigments themselves, it is of importance to consider if there is any culminating point in this aggregation beyond which it is not possible to go.

We have seen that the amount of the change varies with the properties of the pigment, and what might be called the "intensity," and with carbon black a very well-advanced stage is obtained. Can this be reasonably assumed to be the limit of action? There is certainly some suggestion that the effect of carbon black is different from that of magnesium oxide. It is possible that the changes in rubber may show a discontinuity, or stages in some degree analogous to the formation of allotropes of sulfur, phosphorus, etc.

The query appears of further significance in the light of the fact that a definite change takes place in a pure rubber-sulfur mix when a 3% sulfur coefficient is exceeded, and to the fact that selenium and trinitrobenzene cannot vulcanize beyond a certain stage.

3. *The Varying Effects of Pigments and the Varying Maxima.*—The reversal in the amount of Insoluble A formed at a certain percentage of pigment is of much interest. The previous section of this paper dealing with the fall in curves showed that purely mechanical or physical effects could partly bring this about, but it was also concluded that other forces in pigments, as shown in the effects of Kadox against ordinary zinc oxide, also shared in the responsibility for the drop. It becomes a critical point as to whether Insoluble A is produced as a result of the functioning of a set of forces, which may be assumed to be some kind of "surface" energy, and this is continually countered by an opposing force, an electro force which predominates at a certain stage; in fact, while the former increases to a certain fractional exponent with increase in pigments, the latter increases at a faster rate, and this, together with the mechanical effects, produces the sharp fall in the curves.

It is at least logical to conclude that the effect of pigments can be classified into two kinds—one that which would follow on the intrusion of foreign particles into the rubber system, with the consequent alteration to the configuration of the particles, the general surface effect or the increase in total surface and the consequent alteration to the adjustment of the whole system; this action being advanced by the application of pressure, etc. The other kind would be an effect due to the "character" of the interposed particles in respect to their so-called electro properties or electronic arrangement, and the various lines of force.

It is difficult to imagine a perfectly inert pigment, and besides differing in kind the existent forces can also differ in degree. Apparently, therefore, consideration must be given throughout to the inter-pigment particle relations, the inter-pigment to rubber relations, and those of rubber to rubber; the pigment to pigment forces can be expected to involve the pigment to rubber forces; and these considera-

tions appear necessary throughout the study of rubber. Previous reference was made to the similarity of the Insoluble A-forming action of pigment and rubber with colloids in dispersion medium water. While it is not possible here to attempt to apply the multitude of experiments of the latter, it is evident that certain essential facts connected therewith are of particular significance. Thus, for instance, the electro forces in relation to the opposing forces of the dispersions medium increase with the size of these aggregated particles or molecules; and, again, there is the "salting out" with electrolyte of, for example, soap from water; while a third point of much interest is that of the proved effect of the electrification on surface tension, as shown by the capillary electrometer.

Occurrence of Insoluble A in Manufacturing Processes

The foregoing text makes a general comparison of this pectization or Insoluble A effect and the ordinary action of sulfur, and from the data obtained it could be presupposed that Insoluble A would be formed in ordinary compounding procedure. Consequently, from the results of the examination of Insoluble A properties, even regardless of the proved resemblance it shows to vulcanization, it would have to receive consideration in the study of vulcanization, *i. e.*, in accepting vulcanization in the broad sense as the conversion of rubber from a raw state to one of general serviceability. An investigation was made to prove its formation or otherwise, and to ascertain the effects generally.

Even the lowest proportion of compounds used in the experiments described are hardly practicable in ordinary compounding, and yet the lowest proportion used, *viz.*, one of magnesium carbonate to one of rubber, produced only 16% of Insoluble A, and this from rubber masticated only the usual preliminary amount prior to mixing, and not subjected to the plasticizing that the incorporation of the powders in the ordinary process of mixing should bring about. Furthermore, this 16% is still fairly plastic when heated. But, though this is the case, there are obviously other aspects, for in factory mixing on an ordinary mill or mixing machine, though smaller percentages of compounds representing lower pigment surface area are generally used, and the rubber gets more plasticizing than in these experiments, high proportions of pigments equal to those described in the experiments are continually being brought together with the rubber. This action can take place during the enfolding of the rubber on the compound particles, and when the layers of compound or pigment particles and rubber are passing through the nip of the rolls. It is obvious that then the interfacial surface or skin of the rubber must be surcharged with the pigment particles. This action will take place continually throughout the mixing operation. Satisfactory proportions of pigment to rubber for the formation of Insoluble A in well-developed form are, therefore, brought about. The other requirement, *viz.*, pressure, etc., is perhaps more doubtful, owing to the yielding or padding effect of the soft layers of contiguous rubber. It will be recognized, however, that this pressure-reducing effect of the layers of free or unmixed rubber will vary according to the hardness of that rubber, and the sharpness of the impact pressure from the speed and ratio of the rolls. The speed of adding the powders, as well as the ratio of the powders with the "bank" and the thickness of the layer of rubber on the rolls, may influence both factors of the rubber to pigment proportions, and the pressure and stress strain.

The effect of increasing the applicable pressure by hardening the rubber, or reducing its "movability" by cooling and so increasing the particle cohesion, is demonstrated by passing strips of a 45% carbon black master batch cold through cold even speed laboratory rolls about eight times, allowing the strips to cool between

each passing, the pressure being maintained by doubling the strips between each passing. (The carbon black batch was allowed to stand 30 days to "recover" after mixing and before this treatment.)

This rolling has the effect of permanently hardening or pectizing the uncured mixing very considerably. The following table shows the extra masticating, etc., required to bring the rubber again to a calenderable state:

TABLE VIII

Sample Mix	Passed through Mill Rolls		
	Temp., 170° F.	Temp., 190° F.	Temp., 220° F.
Original 45% carbon black mixing	8 times required to produce a good characteristic glossy sheet	6 times required to produce satisfactory glossy sheet	6 times required to produce very fair glossy sheet without sticking to rolls
Orig. mix. 45% carbon black rolled 8 times cold	45 times required to produce even an inferior sheet	At 50 runs, sheet still unsatisfactory	At 50 runs, sheet was still uncalenderable to a smooth state

In each case the pieces of rubber were folded, etc., to obtain the maximum plasticizing effect.

From these results, even though the removal of gases is partly responsible, it can be assumed that an Insoluble A-forming action has definitely taken place, and thus it can be concluded that an Insoluble A-forming or pectizing action can take place in ordinary mixing operations; and with this so, various factory processing troubles can be more easily understood, and many vagaries of rubber mixing are easier of explanation. Thus increased power consumption must be required to plasticize or work the hardened rubber, and consequently there will be an increased tendency to higher temperatures with the increased power absorption. This being so, the rubber will tend more toward temperatures where the sulfur will be affected, and scorching and blooming of the uncured stock becomes more likely. On the other hand, there are factors tending to the reverse effect; for example, the softening caused by increased temperature mostly appears adverse to this action of pectization or aggregation.

Also, it is found that the Insoluble A, when once degraded, produces a rubber of low viscosity or activity, and hence higher fluxing power. Actually, as a result of the hardening of the rubber in the first place, greater energy would be expended on it as a consequence in the process of milling between rolls, especially when the temperature was kept low, and this would explain the final reduction in "liveliness." The 45% carbon black mix after the described milling, when accelerator and sulfur were added, cured to a softer consistency than a normal rubber mix. This, obviously, was due at least to the extra mechanical energy that it would absorb in the act of being milled. Apparently, in ordinary factory compounding, the precautions taken to keep the batch capable of processing actually deal with the prevention of pectization, or the tendency to Insoluble A, or, on the other hand, with its degradation after formation; and in pigment mixes there is apparently a continuous process of aggregation and degradation taking place during mixing, the former increasing with the increase in powders, and yet diminishing with the consequent plasticization from incorporation. In the case of mixes with carbon black, the aggregating intensity of which is so high, small aggregations of rubber and black sometimes remain in the mix, and the formation of this Insoluble A rubber no doubt explains this example of "poor dispersion."

In regard to the effect on the physical strength of the rubber, it is found that well-

developed Insoluble A produces a considerably weaker vulcanizate than the soluble portion. This is seen by compounding Soluble B extract and also Insoluble A with suitable curing ingredients, and testing the resulting vulcanizates. The Insoluble A obtained from a 3:1 magnesium carbonate mix was combined with 5% zinc oxide and sufficient sulfur, diphenylguanidine and stearic acid, and tested alongside Soluble B compounded similarly, with a result as shown in Table IX.

TABLE IX

	Insoluble A Mix	Insoluble B Mix
Breaking strain	43.9 kg. to sq. cm.	183.5 kg. to sq. cm.

The result is significant, and demonstrates how much it is possible for the rubber to be injured as a result of the formation of well-developed Insoluble A and continued milling.

Some allowance must be made for the fact that the Insoluble A portion would be of less purity than the extract because of the probable small residue of acetates and decomposition products, and also for the fact that milling is necessary to incorporate the curing ingredients. Though this was minimized by first swelling in ether, the structure must have been unavoidably further broken down. The results are of particular interest with respect to the previous series of experiments on Insoluble A and vulcanization.

Relation to Mixing Machinery

Incidentally, the results emphasize the importance of the type of mill or mixing machinery on the Insoluble A or aggregating effects. A natural observation is that the theoretically correct machine must incorporate each pigment particle in an amount of rubber matrix agreeing with the proportions shown in the mix formula, and a simple corollary to this would be that the amount of rubber surface exposed to the pigment in a unit time is a basic consideration in judging the efficiency of a mixer, with due regard to the nature of the disrupting forces, cooling, etc.

The foregoing appears to enlarge the field of the compounding art. Wiegand⁶ has previously suggested the "holding back" of the effect of pigments, such as carbon black on rubber, and it seems not improbable that this anti-Insoluble A-forming effect with respect to carbon black or other pigments could be achieved by the use of substances—antipectizers or antiaggregants. Such substances, after functioning in the uncured state, could be duly decomposed by sulfur or other substances, or by heat during the heat of vulcanization, and thus be rendered further inactive. The guanidines and anhydroformaldehyde-aniline possess, no doubt, these characteristics to some degree, but are of course not neutral in curing effects, and the former are poor agers peculiarly enough.

Obviously the search for such substances involves deep-seated problems in the structure of rubber. At this juncture it would appear that an even more effective method of attacking the above problem is in the treatment and preparation of the rubber at the plantation itself.

Insoluble A and Polymerization

The foregoing results are of particular interest in conjunction with certain known facts concerning polymerization of isoprene, such as, for instance, that isoprene polymerizes with varying influences to varying degrees of change. It polymerizes with substances in fine state of division, such as colloidal mercury, and in the above experiments it is seen that pigments in fine state of division with the aid of pressure cause a further change in rubber, the change varying with the pigments until, in the case of carbon black, a very insoluble form of product is obtained.

The action of undefined polymerizing influence, such as heat and pressure on isoprene, actually produces two phases, the actual soft polymerized product itself, and the residual isoprene, and pigments again produce two phases from rubber which may be regarded as actually the transformed and unacted-on fractions, respectively. These facts open up a field for consideration of very much interest and importance.

Synopsis

When pigments are mixed with unmasticated rubber in solution, a certain effect on the solubility of the rubber takes place.

When again these pigments are incorporated in the process of mixing, the mixed rubber dissolves readily in solvents. It is shown in these experiments, however, that when the percentage of pigments is increased to a high degree, a definite change to insolubility again takes place in opposition to the plasticizing effect. The effect of these increased pigments on unmasticated or lightly masticated rubber is still more striking.

This change is mainly brought about on the application of the pressure, and probably stress-strain. By separation of the pigments by acetic acid and ether and treatment of the residue with benzene, the rubber is evidently separable into two well-known defined insolubility fractions.

This Insoluble A product is doubtless to some extent arbitrary, but as shown by certain time-extraction curves the separation into two distinct solubility fractions is unquestionable.

The more insoluble phase is for the sake of convenience called Insoluble A, and the soluble phase Soluble B.

The particle size and specific surface of the pigment is evidently of fundamental importance in the action, but certain physical attributes, such as shape, melting point, etc., modify the effect.

Over a range of different percentages of pigments the Insoluble A produced forms, defined curves; the acuteness of these curves is characteristic of the pigment, and beside certain physical or mechanical effects the fall in insolubility appears to be due to electro charges or the properties of the pigments, as evidenced by the particular charge. Ordinary zinc oxide, for example, which produces a curve of comparatively long plateau, is found to give a negative electrostatic charge, while Kadox zinc oxide, which produces a particularly acute curve, is definitely positive toward rubber. The practical importance of this latter effect is obvious.

The amount of Insoluble A also decreases with the mastication of the rubber, and the effect therein is singularly comparable with the reduction in tensile optimum of the same rubber when mixed with sulfur and vulcanized. The study of Insoluble A, incidentally, throws light on mastication.

Substances such as oil reduce the amount and the physical strength of the product. Little difference is shown in the yield from different rubbers, but the product from *ficus elastica* is somewhat softer than from the *Heveas*. Heat, out of contact with air, causes a gradual reversion of the Insoluble A, but heating in air causes a very rapid degradation.

There is little doubt that the change in rubber may be brought about, and to a pronounced extent, in localized parts in ordinary mixing operations. It is evident the action also proceeds to an extent throughout the entire mass of the rubber product apart from the more intense action at these localized portions, but the plasticizing forces in operation during the incorporation of these powders counters this action, which in any case must be less, owing to the relatively small percentage of pigments ordinarily used in manufacturing procedure.

The severe degree to which rubber may be reduced in physical strength if the Insoluble A action is well developed is shown by the low tensile product of an Insoluble A vulcanizate, compared with a Soluble B vulcanizate.

It is of particular importance that the insolubility of the insoluble, *i. e.*, its hardness and general resistance to solvents, increases with the amount obtained, the 50% Insoluble A from a 2:1 magnesium carbonate to rubber being considerably softer than the 78% obtained from a 3:1 magnesium carbonate mix.

There is some reason for the belief that, besides the pressure, the stress-strain to which the rubber is submitted is also a factor in the formation of the insoluble, and this would afford some light on the nature of elasticity itself as due to a resistance to a molecular change of state induced to take place by the mechanical load.

Apparently the pigment surface is the primary factor in the transformation, and it makes possible the alteration in the equilibrium of the rubber molecule, the effect being that of the concentration of forces of attraction at certain points, the addition of pressure increasing the concentration.

The action of pigments upon the rubber appears to resemble the formation of the usual insoluble fraction in raw rubber, which it is assumed is formed mainly by reason of the non-rubber components, and difference in energy level produced. The amount of sulfur taken up by a rubber converted to Insoluble A is practically the same as that by an untransformed rubber, and this proves again the impracticability of approaching the subject of vulcanization merely from a chemical viewpoint. Certain physical effects from original polymerization, or aggregation, Insoluble A formation, and sulfur are additive. There is some evidence that the product of the action of pigments on rubber, plus a certain amount of sulfur action, shows a somewhat similar susceptibility to bomb aging that the product with a larger amount of sulfur alone does, an important probability that would justify further investigation.

The study of Insoluble A leads to interesting considerations of polymerization and the forces in operation in the structure of rubber. The results throw light on the diphasic properties of rubber and the influences that bring this formation about. The relation to vulcanization is indicated. Further research from the standpoint of Insoluble A should enable additional insight to be made into the problem of rubber from the practical and theoretical point of view, and should also be of value from the viewpoint of colloidal and physical study generally.

What may be termed the *Insoluble A-forming value* of a pigment will be a useful addition to the classified properties of compounds. Certain modifications of the method of production need to be made, however, and this will probably be dealt with at a later date.

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Studies in the Interfacial Relationships between Rubber and Fillers

I. The Tear Resistance of Vulcanized Rubber

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Part IV. The Effect of Small Concentrations of Reinforcing Fillers, on the Tear Resistance of Vulcanized Rubber

As was shown previously (*Trans. Inst. Rubber Ind.*, 8, 379 (1932)), small amounts of a filler have a distinct influence on the tear resistance of rubber. It was decided to investigate this action in the case of the more important reinforcing fillers, and contrast it with their reinforcing capabilities.

Little work on similar lines had hitherto been done. Thus, in the papers describing the tear-testing methods already mentioned, data are also given about the action of some fillers. Evans (*India Rubber J.*, 64, 815 (1922)) gives information on the behavior of fillers in connection with the tearability of rubber, but in his study, criteria such as "smooth-tearing" and "jerky-tearing," depending on the personal element, were taken into account. Magnesium carbonate and china clay were found to decrease the tear resistance, while zinc oxide increased it. Somewhat contradictory results were given by Zimmerman (*India Rubber J.*, 64, 475 (1922)), according to whom all mineral fillers reduce the tear resistance as the volume loading increases. In accelerated (0.5 per cent hexamethylenetetramine) stocks cured with 5.5 per cent sulfur, zinc oxide was found to decrease the tear resistance to a minimum at 7 volumes per 100 of rubber, both across and with the calender grain, whereas further additions of zinc oxide produced increased resistance to tear, the increase being considerably greater across the grain than with it. In fact, with high volume percentages the tearability of the stock was much less than that of the pure gum compound.

Some further information on the matter can be obtained from work by Carpenter and Sargisson (*Am. Soc. Testing Materials*, 2, 897 (1931)), Winkelmann and Croakman (*Ind. Eng. Chem.*, 865 (1930)). They, however, mainly investigated technical mixes, and did not examine the subject of fillers systematically.

The following fillers were included in the determinations undertaken in the present work: carbon black (Micronex), "Thermatomic" carbon black (P-33), zinc oxide (White Seal), light magnesium carbonate, and two grades of refined china clay, "Stockalite" and "Devolite." Of these clays the first is the finer, both being obtained during successive stages of fractional sedimentation of a natural clay.

The determinations were carried out with small concentrations only, for the following reason. At small concentrations the dispersion of the filler in rubber approaches the ideal, by which is meant that every individual particle is surrounded by rubber; consequently, the results of measurements at small concentrations represent more clearly any specific features due to the rubber-filler interface than do determinations with high volume loading, where the interpretation of the results is complicated by the presence of aggregates of flocculated fillers. Furthermore, the testing method described previously (*loc. cit.*) is particularly suitable for measurements on rubber containing small amounts of fillers.

The concentrations of 3, 7, and 13 volumes of filler, respectively, per 100 volumes

of rubber, were chosen for obtaining a range of volume loadings. Incidentally, with zinc oxide a concentration of 25 volumes was tested.

Experimental Details.—The base mixture contained rubber (50 per cent pale crepe + 50 per cent smoked sheet), 100 parts; zinc oxide (White Seal), 5 parts; zinc pentamethylenedithiocarbamate 0.5 part; diphenylguanidine, 0.3 part; and sulfur, 2.0 parts.

In the carbon black (Micronex) mixes the quantity of accelerators was slightly increased (0.52 per cent zinc pentamethylenedithiocarbamate plus 0.31 per cent diphenylguanidine on the rubber in the 7 volumes mix, and 0.55 per cent plus 0.33 per cent, respectively, in the 13 volumes mix). This was done to counterbalance the absorptive properties of the filler, and thus maintain a rate of vulcanization somewhat similar to that of the other mixes. This practice was considered advantageous for obtaining comparable results (Somerville, *Trans. Inst. Rubber Ind.*, 6, 137 (1930)).

All mixes were vulcanized at 125.5° C. for 5, 10, 15, and 20 minutes, respectively. For reasons previously given (*loc. cit.*) the tests were performed on non-grained rubber, though there is no reason to assume that with grained rubber the results would necessarily be exactly the same.

TABLE I
TEAR RESISTANCE IN KG. PER CM. OF VULCANIZED RUBBER MIXES CONTAINING VARIOUS AMOUNTS OF REINFORCING FILLERS. TEMPERATURE OF VULCANIZATION = 125.5° C.

Time of Vulcaniza- tion in Minutes	Base Mix	3 Volumes	7 Volumes	13 Volumes	25 Volumes
		<i>Zinc Oxide (W. S.)</i>			
5	4.60	5.25	8.40	10.20	13.55
10	4.70	7.30	9.50	10.70	13.90
15	5.20	6.30	8.75	10.85	13.20
20	4.60	5.65	8.80	11.50	13.95
		<i>Carbon Black (Micronex)</i>			
5	(As above)	4.05
10		7.50	11.25	14.35	...
15		7.75	11.30	15.20	...
20		6.80	11.60	15.25	...
		<i>Carbon Black (Thermatomic, P-33)</i>			
5	(As above)	5.60	8.20	11.65	...
10		6.75	8.75	11.95	...
15		5.80	8.30	10.75	...
20		6.20	7.60	10.30	...
		<i>L. Magnesium Carbonate</i>			
5	(As above)	4.25	4.50	3.30	...
10		4.80	4.40	3.10	...
15		4.26	4.20	2.35	...
20		4.15	3.50	2.95	...
		<i>China Clay (Stockalite)</i>			
5	(As above)	..	3.70	2.70	...
10		..	3.85	2.80	...
15		..	3.80	2.80	...
20		..	3.80	2.75	...
		<i>China Clay (Devolite)</i>			
5	(As above)	..	3.55	1.95	...
10		..	3.70	2.40	...
15		..	3.65	2.15	...
20		..	3.65	2.40	...

In the previous work (*loc. cit.*) the tear tests were performed at a speed of 20 inches per minute. It was later realized that this was too fast to allow of accurate measurement of the actual width of the sample at the moment of tearing, and therefore the jaws of the machine were separated at the rate of 8 inches per minute.

The results obtained for tear resistance are given in Tables I, II, and III. Each figure is the average taken from eight test-pieces. Table I gives the tear resistance of rubber with each of the fillers examined, at various volume loadings and at different times of cure. Table II gives the ratio of the original width of the test piece to the width at the moment of tearing. Table III gives the corrected tear resistance. Figure I is a graphical representation of the numerical results given in Tables I and III. (For three of the fillers, for which the curves for tear resistance were too close to those for corrected tear resistance, only the latter have been plotted.) Figure 2 shows the comparative effect of the fillers examined over a series of volume loadings. The graphs are plotted from the maximum value measured at each volume loading, selected from the results of Table III.

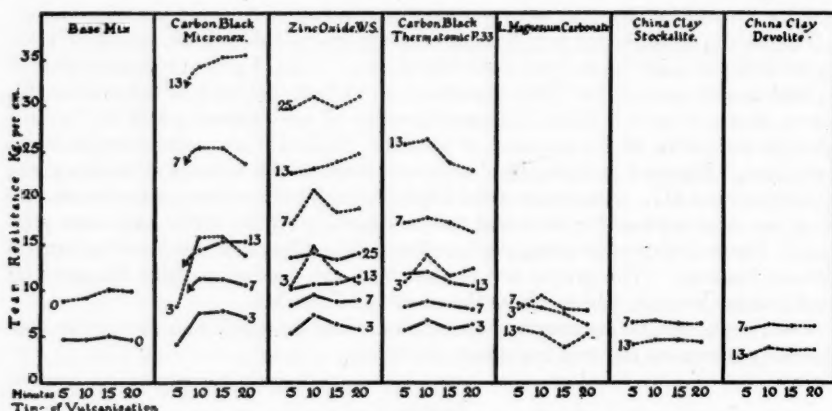
The results can be summarized as follows. Carbon black and zinc oxide considerably increased the tear resistance of rubber.

TABLE II



RATIO OF THE ORIGINAL WIDTH OF TEAR TEST-PIECES TO THE WIDTH AT THE MOMENT OF TEARING, FOR MIXES CONTAINING VARIOUS FILLERS

Time of Vulcanisa- tion in Minutes	Base Mix	3 Volumes	7 Volumes	13 Volumes	25 Volumes
		<i>Zinc Oxide (W. S.)</i>			
5	1.90	1.98	2.03	2.20	2.18
10	1.92	2.02	2.18	2.16	2.20
15	1.96	1.88	2.09	2.20	2.24
20	2.12	1.90	2.12	2.14	2.20
		<i>Carbon Black (Micronex)</i>			
5	(As above)	2.04
10		2.10	2.24	2.39	..
15		2.02	2.24	2.33	..
20		2.01	2.04	2.32	..
		<i>Carbon Black (Thermatomic P-33)</i>			
5	(As above)	1.93	2.10	2.21	..
10		2.03	2.04	2.20	..
15		1.97	2.08	2.20	..
20		1.97	2.08	2.21	..
		<i>Magnesium Carbonate</i>			
5	(As above)	1.86	1.88	1.74	..
10		1.94	1.85	1.71	..
15		1.81	1.77	1.59	..
20		1.84	1.75	1.74	..
		<i>China Clay (Stockalite)</i>			
5	(As above)	..	1.75	1.48	..
10		..	1.71	1.63	..
15		..	1.66	1.61	..
20		..	1.65	1.53	..
		<i>China Clay (Devolite)</i>			
5	(As above)	..	1.63	1.42	..
10		..	1.67	1.54	..
15		..	1.66	1.54	..
20		..	1.64	1.46	..

Of the two grades of carbon black examined, "Micronex" gave the higher figures, while "Theratomic carbon, P-33" behaved similarly to zinc oxide. Magnesium



EFFECT OF REINFORCING FILLERS ON THE TEAR RESISTANCE OF RUBBER

Tear Resistance shown thus: 
Corrected Tear Resistance shown thus: 

Figures accompanying graphs denote volume of filler per cent on rubber.

Figure 1

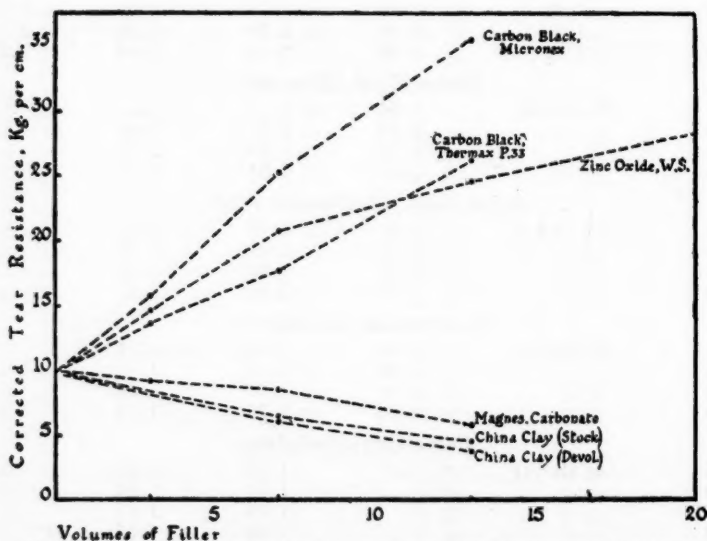


Figure 2—Effect of Reinforcing Fillers on the Tear Resistance of Rubber

carbonate and china clay reduced the tear resistance of rubber, the second having a more pronounced effect. Of the two grades of refined china clay examined, the one having the finer particle size gave higher tear resistance.

TABLE III

CORRECTED TEAR RESISTANCE IN KG. PER CM. OF VULCANIZED RUBBER MIXES CONTAINING VARIOUS AMOUNTS OF REINFORCING FILLERS. TEMPERATURE OF VULCANIZATION = 125.5° C.

Time of Vulcaniza- tion in Minutes	Base Mix	3 Volumes Zinc Oxide (W. S.)	7 Volumes Zinc Oxide (W. S.)	13 Volumes	25 Volumes
5	8.75	10.45	17.20	22.55	29.55
10	9.20	14.65	20.65	23.05	30.60
15	10.20	11.80	18.30	23.80	29.60
20	9.75	10.75	18.65	24.55	30.60
<i>Carbon Black (Micronex)</i>					
5	(As above)	8.25
10		15.70	25.30	34.25	...
15		15.65	25.30	35.20	...
20		13.75	23.55	35.50	...
<i>Carbon Black (Thermatomic P-33)</i>					
5	(As above)	10.80	17.20	25.70	...
10		13.70	17.80	26.20	...
15		11.40	17.30	23.75	...
20		12.20	16.20	22.80	...
<i>Magnesium Carbonate</i>					
5	(As above)	7.90	8.50	5.75	...
10		9.35	8.15	5.30	...
15		7.80	7.45	5.75	...
20		7.65	6.15	5.15	...
<i>China Clay (Stockalite)</i>					
5	(As above)	...	6.50	4.00	...
10		...	6.60	4.55	...
15		...	6.30	4.50	...
20		...	6.30	4.20	...
<i>China Clay (Devolite)</i>					
5	(As above)	...	5.80	2.75	...
10		...	6.20	3.70	...
15		...	6.05	3.30	...
20		...	6.00	3.50	...

Summary

The effect of "reinforcing" fillers on the tear resistance of rubber was examined and it was found that their action was independent of reinforcing properties: carbon black (Micronex), Thermatomic carbon black (P-33), and zinc oxide increased the tear resistance, while magnesium carbonate and china clay reduced it.

II. The Effect of Surface Treatments on Clay as a Rubber Filler

The object of this section of the work was to examine whether it would be possible to alter the characteristics of the china-clay particles in such a way as to maintain the reinforcing capability of this filler, while minimizing its property of reducing the tear resistance of rubber.

The grounds on which the experiments were based were the following.

(a) It has already been found possible to modify the properties of precipitated calcium carbonate as a rubber filler, by coating the particles with a layer of calcium stearate. It has been stated that the tensile strength and the tear resistance of

rubber compounded with this treated calcium carbonate are higher than with the ordinary product because the bond resulting from the system, rubber-calcium stearate, and calcium stearate-calcium carbonate, is stronger than the bond of the rubber-calcium carbonate interface.

(b) The degree of mastication having been proved in another part (IV) of this work to be of importance in regard to the final properties of compounded vulcanized rubber, altering the surface characteristics of the clay might result in change of the behavior of this filler toward the mixing operation, namely, its ease of incorporation in the rubber, and hence elimination of excessive mastication.

(c) Under the assumption that the acicular character of the clay particles is responsible for the reduction of the tear resistance of rubber, it has been suggested that it might be of interest to alter the shape of the particles. (Cotton, *Trans. Inst. Rubber Ind.*, 6, 248 (1930).)

Treatments

All the treatments attempted were of chemical nature, except one which was purely physical. Particulars of the treatments are given below.

No. 1. Precipitating Zinc Hydroxide on Clay, and Converting the Hydroxide into Oxide.—Zinc oxide was anticipated to be an efficient material for the desired purpose, because it increased the tear resistance of rubber (see page 467).

500 g. of china clay (Stockalite) were made into a paste with 500 cc. of a half mol. solution of zinc sulfate. After half an hour, the paste was thinned by adding a litre of water, and then 300 cc. of 0.5 *N* potassium hydroxide solution were added. The amount of alkali was below that theoretically required in order to assure precipitation of colloidal zinc hydroxide which is obtainable in the presence of slight excess of zinc salt. (Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," 1923, IV, 522.)

The mixture of clay and gelatinous zinc hydroxide precipitate was filtered using a Büchner funnel, and redispersed four times in 2 litres of water for thorough washing, with subsequent filtration each time. Finally the mixture was dried at 100° C. and then ground to a fine powder.

The amount of zinc oxide contained in this clay was calculated to be 3-4 per cent of the weight of the clay.

No. 2. Clay Similarly Treated to Obtain a Zinc Oxide Content of about 20 Per Cent.

No. 3. Treatment of Clay with Dilute Hydrofluoric Acid.—This treatment was anticipated to smooth off the edges of the acicular coarser particles, while dissolving some of the colloidal material. 500 g. of china clay were shaken with 1.3 litres of water containing 7 cc. of fuming hydrofluoric acid in a bottle coated with paraffin wax. After 12 hours' shaking, sufficient alkali was added just to neutralize the acid, and the clay was filtered, washed four times with 2 litres of water, and subsequently dried and ground.

No. 4. Precipitating Zinc Stearate on Clay.—500 g. of clay were wetted by 50 cc. of a half mol. solution of zinc sulfate. After half an hour, 1 litre of water was added, and then 95 cc. of one-half mol. sodium stearate solution, a quantity below that theoretically required, so that no free sodium soap was left. The clay with the precipitated zinc stearate was filtered and washed four times by removing each time from the filter and digesting with 2 litres of water.

The zinc stearate thus formed was about 3 per cent, on the weight of the clay.

No. 5. Wetting by Sodium Zincate Solution and Drying in an Atmosphere of Carbon Dioxide.—A solution of sodium zincate was prepared by digesting 130 g. of zinc dust with 105 g. of sodium hydroxide in 200 cc. of water, for two weeks on a steam bath.

400 g. of clay were wetted with 40 cc. of the above solution diluted by 160 cc. of water. The paste was spread in a thin layer on a porcelain dish and dried by gentle heating in an atmosphere of carbon dioxide.

The dried material was then ground and repeatedly washed to remove the excess of alkali. In the course of these washings, any part of clay which settled readily was left aside. The finer part was then dried and ground.

No. 6. Heat Treatment of Clay.—Clay was blown through a flame, so that the plate-like particles might fuse and contract into spherical drops of minute size. The suggestion to carry out this experiment was originally made by F. H. Cotton. It was realized, however, that the pyrochemical properties of clay are such that while speedy dehydration might be expected to occur, causing irregular breaking of the acicular particles, fusion was problematical. The procedure was as follows: A large blowpipe giving, under sufficient air blast, a strong flame about 30 cm. long, was placed in front of a channel $20 \times 10 \times 10$ cm. made of fire bricks. The flame impinged upon the brick wall at one side of the chamber rendering it red hot. The air feeding the blowpipe was passed through a large closed vessel in which a cloud of clay dust was formed and conveyed in a fine stream to the flame.

Great difficulty was encountered in collecting the clay, because, being exceedingly fine, it dispersed in the atmosphere, driven by the gases of combustion. Hence a suction collecting device was employed, consisting of a powerful motor-driven centrifugal fan placed with its funnel facing the exit from the channel and discharging into a bag of finely woven cloth. By using this installation, the clay passing through the flame rebounded from the red-hot wall of the chamber and was collected in the bag. It took six hours for the pores of the sack to become stopped so that a small amount of clay could be collected.

The Treated Clays Tested as Rubber Fillers

The following base mix was used: Rubber (50 per cent pale crepe + 50 per cent smoked sheet), 100 parts; zinc oxide, 5 parts; zinc pentamethylenedithiocarbamate, 0.52 part; diphenylguanidine, 0.33 part; and sulfur, 2.10 parts.

From the above base mix, before addition of sulfur, compounds were made containing 20 volumes each of the treated clays, and to each of them the sulfur was added, together with some dyestuff as explained in a previous section.

For calculating the volume loading of the filler, no correction was made for differences in specific gravity caused by the treatments described, except with clay No. 2 which contained a large amount of zinc oxide. The specific gravity of this clay was found to be 2.9, and corresponding allowance was made in the mix.

For the sake of comparison, a blank mix was made, using the refined china-clay (Stockalite) on which the various treatments were tried. The blank mix has been denoted "O." The mixes were vulcanized at a temperature of $125.5^{\circ}\text{C}.$, two times of vulcanization being employed.

The objection may arise that two times of vulcanization do not give sufficient information as to the properties of the various mixes, considering that the treatments may have had some influence on the rate of vulcanization. In this case it must be explained that the differences in properties looked for were of such an order that variations caused by slight differences in the degree of vulcanization would not alter the results.

The results are given in Table IV and partly in Fig. 3. The latter is an approximate representation of the comparative effect of the treated clays on the tear resistance of rubber, since the graphs were plotted from the figures for tear resistance of the 20 volumes clay mixes and tear resistance of the base mix, which was deter-

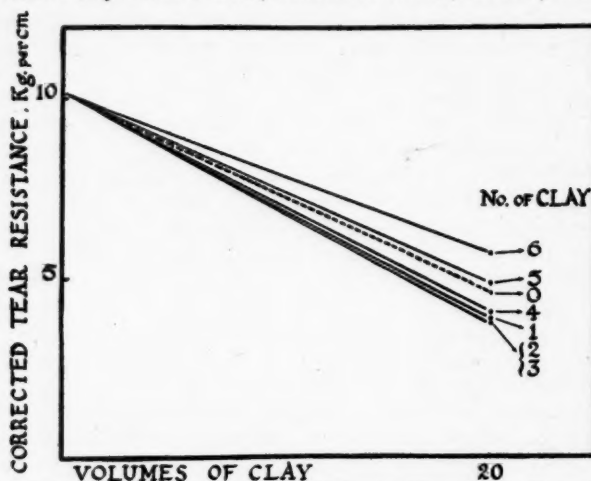


Figure 3—Comparative Effect of Treated Clays on the Tear Resistance of Rubber

mined separately. (Ten minutes cure: tear resistance 5.25, corrected tear resistance = 10.25, 15 minutes cure: tear resistance = 4.80, corrected tear resistance = 9.85.)

TABLE IV
MECHANICAL PROPERTIES OF RUBBER MIXES CONTAINING 20 VOLUMES OF THE TREATED CLAYS

Time of Vulcanization in Minutes	Tensile Strength	Elongation at Break	Modulus at 400%	Tear Resistance	Corrected Tear Resistance	Tensile Strength	Elongation at Break	Modulus at 400%	Tear Resistance	Corrected Tear Resistance
			No. 0					No. 1		
10	192	596	84.3	2.65	4.60	172	590	80.0	2.35	3.70
15	200	590	90.5	2.60	4.35	193	590	88.4	2.40	3.90
			No. 2					No. 3		
10	173	580	78.0	2.25	3.60	187	582	78.4	2.30	3.60
15	188	571	82.3	2.36	3.80	187	570	87.6	2.30	3.80
			No. 4					No. 5		
10	177	603	70.1	2.65	4.10	204	582	96.0	2.75	4.85
15	190	600	82.0	2.35	3.85	210	592	99.3	2.75	4.75
			No. 6							
10	191	560	101.4	3.20	5.75					
15	194	562	103.2	3.10	5.50					

These points were joined by straight lines for the sake of simplicity, though the real form of the graphs, if intermediate volume loadings had been determined, would be similar to that of the curves in Fig. 10. It was believed that this arbitrary method would not interfere with the presentation of the results.

It will be seen that only small differences in properties were obtained by the treatments described. From the viewpoint of effect on the tear resistance, Clay No. 6 (pyrotreatment) gave the highest results, while four clays, Nos. 1 to 4, had a slight diminishing effect on the tear resistance.

Clay No. 4 (precipitation thereon of zinc stearate) behaved differently from any other during compounding.

It is recognized that clays are difficultly "wetted" by rubber, and their incorporation in a mix is a long process. However, with Clay No. 4 compounding on the mill was remarkably rapid. The extent of this difference may be gaged from the duration of mixing: for untreated clay, and most of the treated samples, seven to nine minutes' milling was required for incorporation of 20 volumes in the rubber, while Clay No. 4 was satisfactorily dispersed after milling for three to four minutes, and no tendency to form flakes could be noticed.

Summary

Experiments were carried out with a view to modifying the properties of china-clay as a rubber filler. Of six treatments described none gave outstanding results; though a noticeable effect was obtained by passing clay through a flame, which resulted in increase of the tear resistance of mixes containing that clay.

III. Properties of Vulcanized Rubber Prepared from Compounded Latex

In this section of the work an outline is given of the characteristics of the system "latex rubber"-filler, contrasted to those of "masticated rubber"-filler.

It will be understood that by "latex rubber" is meant a product prepared from latex without mechanical mastication.

The general method of preparing compounded rubber of this kind is to mix latex with a dispersion of fillers and (usually, but not always) vulcanizing agents; by suitable separation of the dispersed phase from the dispersion medium (water) a compounded rubber is obtained. There are several methods for separating the dispersed phase of compounded latex, and among these can be mentioned evaporation of the water, thickening of the dispersion and subsequent drying, electrophoretic processes, coagulation by acids or by heating (heat sensitized latex). Latex rubber is known to possess enhanced wearing properties and particularly good resistance to aging. Its water absorption is higher than that of ordinary rubber, and its behavior toward organic solvents is also different.

The chief reason for which latex rubber has distinctive characteristics is that the rubber has not undergone disaggregation and changes due to mechanical mastication (by action of oxygen, heat, etc.). Furthermore, latex rubbers vary according to the nature of the particular latex used (preserved or concentrated), and show also differences due to causes inherent in the methods by which they have been prepared.

Satisfactory vulcanized samples were obtained for a pure gum mix and a clay mix, but by the method followed, carbon black dispersion in the rubber was not achieved.

To prepare latex rubber free from aligned elements, rubber latex was mixed with dispersions of the fillers and vulcanizing agents and then spread in the form of a thin layer to dry. The sheet obtained was built up to the thickness required for test-pieces and vulcanized in a hydraulic press. The vulcanizing agents were mixed with the latex in the form of a paste of the following composition, by weight: Colloidal zinc oxide (Kadox), 50 parts; flowers of sulfur, 22 parts; zinc penta-

methylenedithiocarbamate, 5 parts; mercaptobenzothiazole, 2 parts; ammonium oleate (5 per cent solution), 30 parts; casein (10 per cent solution), 3 parts; and water, 66 parts.

The paste was ground in a paint mill for two hours. The fillers were also made into a paste each by grinding in a paint mill with water and a dispersing agent. The latex used was a concentrate containing 75 per cent dry solids.

The following gives the details of the mixes.

(1) *Pure Gum Mix*.—1330 g. of concentrated latex (= 1000 g. of dry solids) were diluted with 125 cc. of water. 178 g. of the vulcanizing paste were dispersed in 125 cc. of water and then added to the diluted latex. The mix was stirred for ten minutes and then spread on clean glass plates in the form of a thin layer, for drying.

(2) *Fifteen Volumes Clay Mix*.—178 g. of the vulcanizing paste were dispersed in 180 cc. of water. 425 g. of china-clay (Stockalite) were dispersed in 600 cc. of water containing 3 cc. of a 5 per cent ammonium oleate solution. The two dispersions were mixed together and then added to 1330 g. of concentrated latex, after which the whole mix was stirred for ten minutes and then spread for drying.

TABLE V
PROPERTIES OF VULCANIZED RUBBER PREPARED FROM COMPOUNDED LATEX

Time of Vulcaniza- tion in Minutes	Tensile Strength	Elongation at Break	Modulus at 400%	Tear Resistance	Corrected Tear Resistance
<i>Base Mix</i>					
5	255	752	35.6	7.15	14.45
10	232	700	37.6	6.30	11.90
15	204	684	38.0	6.05	9.75
<i>15 Vols. Clay Mix</i>					
5	323	658	85.5	5.05	10.30
10	234	632	88.4	5.80	9.95
15	207	590	90.0	5.35	8.65

(3) *Fifteen Volumes Carbon Black (Thermatomic P-33) mix*.—The mix was made similarly to the clay mix, 282 g. of "Thermatomic" carbon black being taken to give 15 volumes.

The composition of the vulcanizing paste as given above corresponds to 1000 parts of dry solid contents of the latex, and the percentage composition of the mixes can thus easily be seen.

In this connection it will be noticed that instead of diphenylguanidine, which was found a very suitable secondary accelerator in the type of base mix largely used with masticated rubber, mercaptobenzothiazole was here employed, because a water dispersion of diphenylguanidine was found in these experiments to cause a remarkable gelling of a thin dispersion of clay, turning it to a thick and stiff pasty consistency, which rendered dispersion in latex impossible. It would appear of interest to investigate this action of diphenylguanidine.

The mixes described above were dried for five days, in a current of air. The dried sheets had no stickiness, and in order to ply up several layers, their surface was rubbed with a cloth slightly moistened with benzene; satisfactory adhesion was thus obtained, and plates of about 7 mm. thickness were built up. From these plates, discs of the size of the Schopper ring molds were cut and vulcanized in the press.

In the desire to carry out these experiments in a way enabling a comparison of the results with those obtained with masticated rubber, the base mix used was similar

to the base mixes of corresponding sets of tests, with the ordinary milling procedure. It was, however, found subsequently, by some preliminary vulcanizing tests, that the accelerating influence of the non-rubber components of the latex employed had not been duly estimated, and the percentage of accelerators put in the base mix resulted in a very fast curing compound. Hence the temperature of 110° C. was used for vulcanization.

The Thermatomic carbon black mix failed to give vulcanized products of any value. Examination showed that there had been no dispersion of this filler in the rubber, since the black rubbed easily from the sample. The mechanical properties of the product were poor, as is typical of bad dispersion.

The results for the other two mixes, pure gum and clay compound, are given in Table V.

The mechanical properties of both mixes indicate that the base mix used was a very fast curing one. The tensile characteristics of both mixes were slightly superior to those of similar analogous mixes with masticated rubber, given in this work. Both latex mixes were distinctly superior with regard to tear resistance.

Summary

Experiments were made with latex. The properties of a "pure gum" mix and a rubber-clay mix prepared from compounded latex were found superior to those of similar mixes made in the ordinary way, the tear resistance of latex rubber being particularly high.

IV. The Effect of Mastication on the Properties of Vulcanized Rubber

The influence of mastication on the properties of unvulcanized rubber has been the subject of extensive experimental work in recent years.

As the elastic properties of unvulcanized rubber are profoundly affected by mastication, interest has also been given to the effect of mastication on the properties of rubber after vulcanization.

It is recognized that most of the effects brought about by mastication on unvulcanized rubber, disappear during vulcanization. Nevertheless, the degree of mastication was found to exert a certain influence on the rate of vulcanization, the tensile strength, etc. (See Wiegand, *Trans. Inst. Rubber Ind.*, 7, 422 (1932); Usherwood, *ibid.*, 7, 227 (1932).)

During the present investigation it was noticed that differences in the milling procedure when compounding had an influence on the tear resistance of rubber, while little effect if any could be noticed on other properties.

Mastication of rubber, being a treatment closely associated with structural changes, it was thought that its influence might be particularly pronounced on those properties of rubber in which structural features are especially involved. Hence it was decided to carry out a series of determinations with purpose to elucidate this view.

The effect of mastication was measured on a pure gum mix and also on a mix containing 20 volumes of china clay. In this way any specific effect of the filler in this connection would be noticed.

The mixes used were:

(1) *Pure Gum Mix* containing rubber (50 per cent pale crepe + 50 per cent smoked sheets), 100 parts; zinc oxide, 5 parts; zinc pentamethylenedithiocarbamate, 0.53 part; diphenylguanidine, 0.33 part; and sulfur, 2.2 parts.

(2) *Clay mix*, which was the base mix, with 20 volumes china clay (Stockalite) per cent on rubber.

The procedure was as follows: (1) *Pure gum mix*. A large batch of rubber (1.5 kg.) was masticated in an internal mixer (Bridge-Banbury, laboratory size), at a temperature of 120° C., for 2.5 minutes. At the end of this time the zinc oxide and the accelerators were added in form of a master batch (concentration 58.5 per cent), which was previously made on open mill at high temperature to avoid over-milling the rubber. Milling in the internal mixer was carried on for another

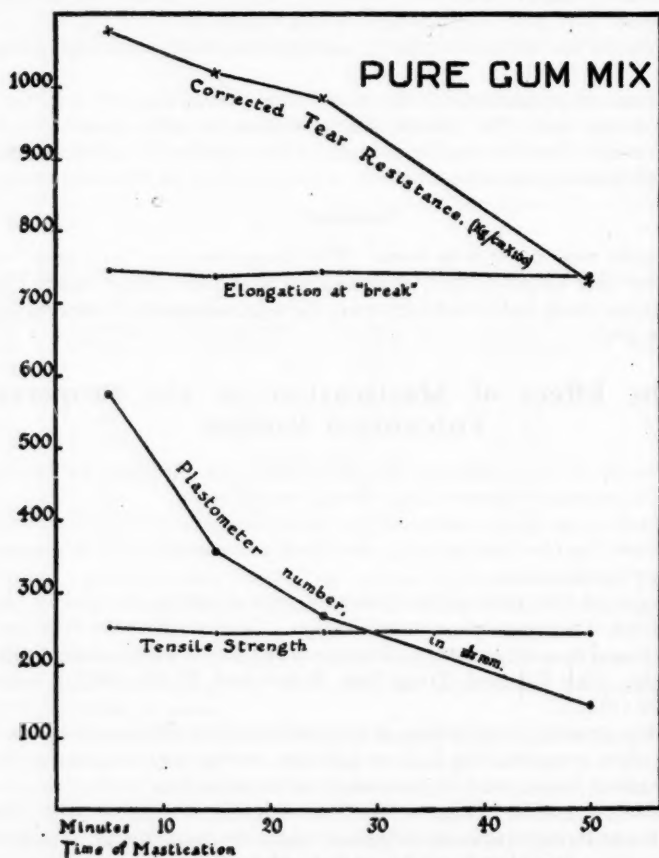


Figure 4—Effect of Mastication on a Pure Gum Mix

minute by the end of which the master batch was completely mixed with the other rubber. The whole batch was taken from the internal mixer and divided into four equal parts. One of these was transferred to an open mill at a temperature of about 40° C., and a sample of definite weight (35 g.) was taken for the plasticity test, after which sulfur corresponding to the remaining rubber was added to make up the complete mix. The mixing of the sulfur lasted 1.5 minutes. The three other parts of the batch were masticated on the open mill at 40° C. for 10, 20, and 45 minutes, respectively, and by the end of the milling a sample for plasticity test

TABLE VI
THE EFFECT OF MASTICATION ON THE PROPERTIES OF VULCANIZED RUBBER

Unvulcanized Mixes	Plasto- meter No.	Time of Thick- ness in Mastication 1/100 Min.	Tensile Strength, Kg.				Elongation % at Break				Vulcanized Mixes, Time of Cure in Minutes				Tear Resistance, Kg. per Cm.				Corrected Tear Resistance, Kg. per Cm.			
			5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
Pure gum	5	576	236	253	242	226	781	745	746	681	27.0	28.7	32.3	32.8	5.35	5.45	5.30	5.30	10.60	10.70	10.20	10.40
mix	15	357	240	245	249	237	807	738	723	715	19.3	27.2	29.9	29.4	4.90	5.15	5.05	5.10	9.50	10.20	10.20	10.00
	25	266	228	246	251	238	802	742	710	706	18.7	26.5	29.8	29.0	4.90	5.05	5.15	5.05	9.05	9.85	9.80	9.75
	50	142	201	231	242	232	837	745	736	721	15.3	23.8	28.0	28.2	3.85	4.00	4.05	3.90	6.70	7.20	7.30	7.15
20 volumes 10% clay	8.5	463	229	233	242	236	589	586	580	582	103.2	109	117.5	123	3.95	3.95	3.85	3.60	7.10	7.15	6.85	6.40
	15	420	204	222	239	240	594	588	584	579	82	97	105	108	3.15	3.25	3.25	3.20	5.55	5.70	5.65	5.30
	25	322	193	202	222	217	586	584	584	578	73	84.5	98	101	3.00	2.85	2.75	2.80	4.90	4.90	4.75	4.65
	50	266	183	194	220	227	600	592	598	581	63.8	81.5	95	98.2	2.20	2.30	2.35	2.25	3.70	3.95	4.00	3.92
^a In nitrogen.		178	111	143	168	185	643	598	599	601	38.4	64	71	76.5	1.45	1.60	1.65	1.60	2.15	2.50	2.75	2.60

was taken and the sulfur mixed in, with consequent working of one and one-half minutes. The total milling times of the four mixes were thus: 5, 15, 25, and 50 minutes. The surplus mastication given to the batches during the mixing of the sulfur after the samples for plasticity tests were taken is assumed of no appreciable effect on the results.

(2) With the clay mix, analogous procedure was applied which involved mastication of the rubber in the internal mixer for 2.5 minutes; addition of the zinc oxide and accelerators master batch; milling for another minute; addition of the clay, and further milling for 3.5 minutes. The remaining operations were similar to those described for the pure gum mix. The total times of mastication for the clay mixes were 8.5, 15, 25, and 50 minutes.

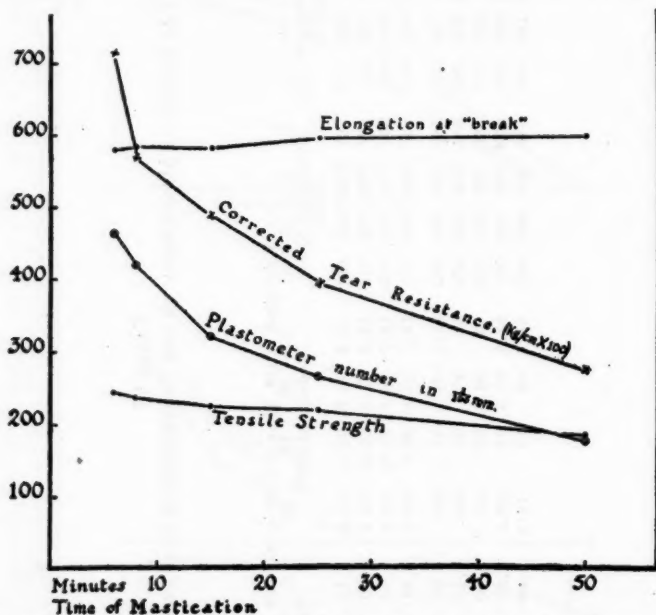


Figure 5—Effect of Mastication on a Rubber-Clay Mix Containing 20 Volumes of China Clay

The first stocks in both series represented mixes masticated for shorter time than in the usual compounding practice, while the ones masticated for 50 minutes were definitely overmilled.

In parallel with the above series, a clay mix was made in the internal Bridge-Banbury mixer in an atmosphere of nitrogen, which according to recent investigations minimizes the breaking-down of the rubber.

The milling time for each stock gives some indication of the degree of mastication, though it should not be overlooked that the first stocks of each series, intended to be as little masticated as possible, were milled at higher temperature than the other ones. For more exact information, a measure of the plasticity of the stocks was determined.

Plasticity measurements on the unvulcanized samples (not containing sulfur) were carried out at 70° C. one week after mixing. The figures given are the thick-

nesses in 0.01 mm. of 2 cc. pellets in a parallel plate plastometer after 5 minutes' loading with 5 kg.

To account for differences in vulcanizing properties due to dissimilar mastication, the tests for vulcanized rubber were made on samples vulcanized over a range of four curing times, at the temperature of 120° C. The results of the measurements on the vulcanized samples together with data on the conditions of the respective unvulcanized stocks, are given in Table VI, and partly in Figs. 4 and 5. The figures contain graphs showing the mechanical properties of the vulcanized mixes (tensile strength and elongation at break at the optimum vulcanization, maximum tear resistance) as compared with the stiffness (plastometer number which is the reverse of plasticity) of the respective unvulcanized stocks.

The mechanical breakdown of the rubber in the mix compounded in nitrogen was much slower than in the case of normal milling; hence in plotting the plasticity figures, it was considered admissible to extrapolate the curve relating plastometer number with time of mixing of the air-milled samples, and indicate on that graph the determined plastometer number of the nitrogen-milled sample, thus assuming that mixing in nitrogen gave the same degree of rubber breakdown as in the thus indicated shorter time in air.

The results can be summarized in the following:

Excessive mastication of a pure gum mix had little effect on the tensile strength, but reduced to some extent the tear resistance. In a clay mix, overmastication caused a notable lowering of the tensile strength, and a much more pronounced diminution of the tear resistance. In both types of mixes, overmastication brought about a retardation of vulcanization, noticeable by a displacement of the maximum tensile strength toward longer curing time.

Summary

The effect of mastication during compounding on the properties of vulcanized rubber was determined, and it was found that pronounced mastication had a remarkably adverse effect on the tear resistance of rubber, while other mechanical properties were little affected.

General Discussion and Conclusions

Theories hitherto advanced to explain the phenomena of tearing in compounded rubber have been shown inadequate. If tearing were exclusively due to alignment of anisotropic particles, it would be reasonable to expect, by analogy with other grained or lamellar materials (wood, mica, etc.), that practically no tearing would be possible across the grain of calendered rubber, and in the case of a highly reinforcing anisotropic filler, *e. g.*, china clay, the tear resistance of rubber-clay mixes across the grain might be expected to approximate to that of rubber-carbon black mixes.

It was not a matter of experience that in grained rubber-clay mixes tear resistance across the grain reached such high values, and quantitative differences between tear resistance across and in the direction of the grain remained to be determined by experiment.

That the phenomena of tearing could not be considered as explained by the assumption of lamellar structure was supported by Twiss (*Trans. Inst. Rubber Ind.*, 2, 78 (1926)), who in discussing the importance of particle character in a rubber pigment, stated that among the advantageous effects imparted by certain powder particles, resistance to tear and "knottiness" were well recognized, but their explanation was not obvious.

The impossibility of devising a perfect method for determining a phenomenon,

the nature of which is as yet so obscure, was realized, and it was thought that the method described, provided that its limitations be borne in mind, could be a useful instrument in enabling information on the fundamental features of tearing to be gathered. Accumulation of such knowledge should contribute in developing more accurate testing methods.

Grain Effect and Tear Resistance (*Trans. Inst. Rubber Ind.*, **8**, 377 (1932)).—The experiments described in connection with measurements of tear resistance of rubber in the direction of and across the calender grain have shown that: (a) all fillers contribute to the formation of grain, which is persistent after vulcanization; (b) if the magnitude of the grain effect (difference in properties in different directions) be judged by the tear resistance; china clay, a typically anisotropic filler, gave small difference in tear resistance along and across the grain, whereas zinc oxide, referred to as a typically isotropic filler, caused such great difference that no tearing across the grain of calendered rubber containing this filler could be obtained. [It is shown in Table II of the previous paper that a grained mix containing 20 volumes of china clay gave an average tear resistance 1.88 kg. per cm., the respective values across and with the grain being 2.03 and 1.74. A zinc oxide mix of similar concentration, though overcured, gave the value 6.2 for tear resistance in the direction of the grain; the anisotropy, however, was so pronounced and the resistance across the grain was so high that tearing always followed the direction of the grain and measurement across it was not possible.] Consequently, it is erroneous to infer that the presence of strong grain effects in a vulcanized rubber compound necessarily implies weak tearing. This is clearly shown in grained zinc oxide and carbon black mixes.

It has been shown that the view that anisotropic fillers reduce the tear resistance of rubber by causing grain is not fully substantiated by experiment.

Measuring the Tear Resistance of Rubber (see *Trans. Inst. Rubber Ind.*, **8**, 364 (1932)).—In a review of the present methods for measuring tear resistance, their chief characteristics were mentioned. It is evident that most of the methods constitute technical tests.

An attempt to examine tear resistance of rubber in a methodical way, resulted in developing a testing method for a logical representation of the results based on the metric system of units and taking into account the deformation of the test-piece.

From a comparison of the figures given in the two papers it will be seen that there is a noticeable parallelism between tear resistance and corrected tear resistance; either expression being taken, the relative magnitude of the results remains the same. It is true, however, that small differences between figures become more evident if expressed as corrected tear resistance.

The new method developed is not claimed to render the determination of tear resistance as accurate as the measurement of other properties of rubber.

Effect of Reinforcing Fillers on the Tear Resistance of Rubber.—The results of the experiments described have clearly shown the relative effect of reinforcing fillers on the tearability of rubber, and have confirmed the opinion that certain among them reduce the tear resistance. In any attempt to relate the results with the anisotropy of the filler particles, the following remarks will be of interest.

Typical anisotropic fillers reduced the tear resistance; the fillers found to increase tear resistance are among those generally referred to as isotropic.

The relative extent of particle anisotropy between china clay and light magnesium carbonate is not precisely known. Vogt and Evans (*Ind. Eng. Chem.*, **15**, 1019 (1923)) basing calculations on figures for Poisson's ratio, came to the conclusion that the dimensions of a typical clay particle (length, width, and thickness) are

approximately as 5:2:1. Microscopic observation reveals a distinct acicular character for magnesium carbonate particles; the special refined china clay examined (Stockalite) does not show clearly defined plate-like particle shape; it should not be overlooked, however, that in the case of china clay, there is a great percentage of submicroscopic particles which are responsible for the action of this filler, and little can be said about the shape of these invisible particles. (Pohle, in "Memmler's Handbuch der Kautschukwissenschaft," p. 734.)

Of the two grades of carbon black examined, ordinary gas black gave higher tear resistance than Thermatomic carbon. The latter, as proved by the microscope consists of almost spherical particles, while there is no such proof for the former, for which, rather, indications exist that it consists of both isotropic and anisotropic particles. (Parkinson, *Trans. Inst. Rubber Ind.*, 5, 263 (1929).)

Therefore, although there was a broad relationship between particle shape of the fillers examined and their respective effect on tearability, it does not seem justifiable to explain the phenomena of tearing purely on grounds of particle anisotropy.

The Tearability of Rubber-Clay Mixes.—From an examination of the results obtained throughout the work, it is evident that means are available whereby the tear resistance of rubber-clay mixes may be controlled within limits. Thus for a mix containing 20 volumes of clay, widely differing figures for tear resistance have been obtained, according to the base mix, the accelerator used, the temperature of vulcanization, the process of preparing the mix, etc. As an example, the following results show the tear resistance of a rubber-clay mix (20 volumes clay) under various conditions:

	Kg. per cm.
(1) With ethylidene-aniline condensation product vulcanized at 147° C.	1.65
(2) With zinc pentamethylenedithiocarbamate and diphenylguanidine, overmasticated, vulcanized at 120° C.	1.65
(3) Ditto, normally masticated, vulcanized at 125.5° C.	2.56
(4) Ditto, masticated in nitrogen, vulcanized at 120° C.	3.95
(5) With zinc pentamethylenedithiocarbamate and mercaptobenzothiazole mix prepared from latex (15 vol. clay) vulcanized at 110° C.	5.85

By adopting procedures thus shown advantageous, the value of china clay as a rubber filler can be considerably increased.

Surface Treatments of Clay.—It was shown in Table IV and Fig. 3 that the treatments attempted with a view to modifying the properties of china clay as a filler, had little effect, the highest tear resistance obtained (treated clay No. 6, tear resistance, 3.20 kg. per cm.; corrected tear resistance, 5.75) being less than 30 per cent above that of the mix containing untreated clay (tear resistance, 2.65 kg. per cm.; corrected tear resistance, 4.60), while by control of mixing procedure, etc., as described above, differences as high as 250 per cent were reached.

The results of the treatments Nos. 1, 2, and 5 may be explained by assuming that the substances precipitated on the clay did not really coat the clay particles, as anticipated, but merely formed coarse aggregates which diminished the strength of the vulcanized mix.

Treatment No. 4 can assuredly be considered as coating if its effect in shortening the milling time be considered. With regard to the properties of the vulcanized mix no indication of increased bond between rubber and clay is apparent.

It may be mentioned that Boiry (*Revue Générale du Caoutchouc*, 8, 108 (1931)) has also attempted to modify the properties of fillers, by changing their electric charge; his suggestion being that electric charge phenomena are mainly responsible for re-

inforcement. With one of three treatments attempted, namely by treating electronegative fillers by weak alkali, he noticed a slight improvement of the properties of certain fillers (kaolin, lamp black, silica, etc.). He was not able, however, to ascertain whether this improvement was due to the degree of division of the fillers. There is scope for further research along these lines.

The System: Vulcanized Rubber-Filler.—Reinforcement, in the sense of increased energy absorptive capacity, has little bearing on either energy storing capacity or the wearing capability of rubber. If it be recalled that the latter is generally attributed to strength in the bond between rubber and filler, it will be understood that reinforcement is not directly related to this interfacial affinity between rubber and fillers, but is of a complicated nature.

The following seems a tenable explanation of reinforcement. On reinforcement by a filler such as carbon black, for which a multitude of facts indicates high attractive force toward rubber, the increased work required for the extension of the compounded rubber to rupture is consumed to overcome (i) the high free surface energy of the system, which is opposed to separation of the two phases, and (ii) a component which will be assumed of complicated nature. This is in agreement with present views on reinforcement, particularly if factor (ii) be denoted as frictional losses.

In the case of a filler such as clay, however, for which indications from effects other than resilient energy do not support the assumption of a high attractive force toward rubber, (i) must be regarded as small, while component (ii) will be considered of exceptional magnitude.

It was noted above that component (ii) is assumed to be of manifold nature. The following factors probably contribute: frictional losses, and mechanical characteristics peculiar to fibrous systems (cf. increased strength of thin films, drawn wire, etc.). From this aspect, anisotropic fillers may have a more pronounced effect, since they produce a fibrous structure, and hence may manifest great resilient energy owing to factor (ii), though not to (i).

It is remarkable that fine anisotropic fillers generally possess reinforcing properties; apart from magnesium carbonate and clay, talc has been found as clearly showing reinforcement (unpublished work), and of two grades of barytes, Vogt and Evans found that a special anisotropic sample had greater reinforcing effect than the ordinary material (*Ind. Eng. Chem.*, 15, 1019 (1923)). Attempts have been made to explain the mechanism of this reinforcement by anisotropic fillers (Endres, *Ind. Eng. Chem.*, 16, 1149 (1924)).

Grain Effect. Suggested Mechanism of Tearing.—The experience with grain effect, described in the present work, supports the conception just outlined. Grain is dual in origin. Part is caused by alignment of anisotropic fillers, and is persistent after vulcanization; part is due to alignment of rubber fibrils. There has been controversy as to the persistence of grain due to the rubber, and though Wiegand and Braendle have shown (*Ind. Eng. Chem.*, 15, 259 (1923)) that it is persistent if the conditions during vulcanization do not allow distortion, some still hold that grain due to the rubber phase disappears during hot vulcanization. The experiments mentioned substantiate the views of Wiegand and Braendle, and moreover indicate that grain due to the rubber phase can, under suitable conditions, be as strongly pronounced as that due to anisotropic fillers. This was found with a zinc oxide mix of high concentration.

In considering the mechanism of tearing, the links between the elements of the rubber network (consisting of fibrils, micelles, multiple spiral chains or bundles of macromolecules) may be assumed weaker than the internal cohesion of the fibrils.

These relatively weak spots may be attacked by oxygen during mechanical working, and result in the familiar disaggregation and softening characteristic of masticated rubber. Vulcanization evidently restores the framework by aggregation, but the links between the fibrils always remain frail spots in the structure. Whatever the nature of these links may be, it seems reasonable to assume that forces of attraction are mainly located at the ends of the fibrils. Thus on calendering or stretching rubber, the fibrils are aligned by a moment of rotation, and grain is developed. The greater part of the attractive forces of the fibrils is concentrated at the links in the continuation of their length, while a smaller amount binds the fibers sideways. Hence in grained rubber any plane parallel to the fibers will be a plane of but moderate resistance. Whether the rubber be grained or not, rupture in the network may be assumed to occur at the links between fibrils. If breaking occurs in some part of the network of a rubber mix, and a pull is applied to that place, the rupture will proceed from link to link and result in what is known as tearing.

Two cases are possible in compounded rubber: (a) rubber mixed with a filler for which it has great affinity; and (b) rubber mixed with a filler for which it has little affinity.

(a) Filler particles are embedded in the rubber, and cause an increase in the strength of the network. If some of the filler particles be assumed to play the role of links between fibrils, it will be understood that in a grained rubber of this type there will be a marked increase in strength of bonding between planes across the direction of the fibers, while in a plane parallel with the fibers the increase will be comparatively small. More pull will be required to tear rubber containing such a filler.

If the rubber be grained, the tear resistance across the grain will be exceedingly high, while along the grain it will be smaller, but always higher than in a pure gum mix. Typical examples of this were found in mixes containing zinc oxide and carbon black, vulcanized compounds of which show increase both in tensile strength and tear resistance.

(b) The filler embedded in rubber reduces the strength of the bond in the network. Filler particles are interposed between fibrils and result in a link weaker than that between the rubber fibrils themselves. Moreover, if the filler be anisotropic there may be planes of weak cohesion parallel to the longest dimension of the particle, since in these planes there will be a greater proportion of rubber-filler interface. The tear resistance along the grain will be less than that across it. Mixes containing magnesium carbonate or china clay were considered to be examples of this type.

The increased tensile strength and resilient energy of such mixes must be explained by thin film formation and increased friction due to anisotropic particles, respectively.

A corollary of this statement would be that fillers which have little affinity for rubber and at the same time cannot give rise to mechanical effects such as friction, lamination, etc., must reduce both the tear resistance and the tensile strength of rubber. A filler of such behavior, not included in the present investigation, would be factice (vulcanized oil). Microscopic examination of mixes containing factice reveals minute particles of this material dispersed in the rubber (Pohle, *loc. cit.*). These particles being deformable cannot contribute to frictional effects, etc., and hence they lower not only the tear resistance, but the tensile strength of rubber.

Effect of Mastication.—The necessity of assuming a network structure to explain the tearing of rubber has been emphasized. Such a conception finds support in the decrease of tear resistance of vulcanized rubber by increasing the degree of

mastication before vulcanization. The mechanism of mastication has recently been the subject of investigation, and the role of oxygen is recognized. (A comprehensive review is given by Dufraisse, *Revue Générale du Caoutchouc*, 9, No. 85, 4, No. 86, 3 (1932).) It must be assumed that this disaggregating action of oxygen is not merely catalytic but that some oxygen combines, and its effects do not completely disappear during vulcanization. It seems probable that oxidation products affect adversely the linkage between fibrils, and result in a decrease in the cohesion of the network. Rubber fillers being by absorption air carriers accentuate this destructive influence of mastication. Moreover, coarse or edged particles are likely to affect this destruction during mastication, in a purely mechanical manner.

Though with the pure gum mix examined, no decrease in tensile strength by mastication was noticed, the results with the clay mix, in agreement with Wiegand's findings (*loc. cit.*) indicate that the tensile strength is also impaired to some extent. In Wiegand's work this became especially evident after aging.

Measurements of tear resistance promise to reveal structural features of rubber which escape detection by tensile measurements or only affect them after aging. Suitable determinations of tear resistance may obviate the need for artificial aging tests.

A particularly interesting feature of the graphs obtained in the experiments on mastication is that if the curves for corrected tear resistance be extrapolated toward the range of shorter mastication periods, they cross the axis of tear resistance (mastication = 0) at points approximating to the values of tear resistance found for the latex mixes.

Rubber Prepared from Compounded Latex.—The figures obtained for tensile strength and ultimate elongation of the latex mixes seem to indicate that the vulcanized products did not represent the best types obtainable. Despite this, the figures for tear resistance exceeded all values given by masticated-rubber mixes, thus showing that high resistance to tear is a typical characteristic of compounds which have not undergone a destruction of the rubber network by mastication. The links between the rubber fibrils being unimpaired, the total length of the fibers can be assumed greater than in masticated rubber. Moreover, due to the fact that no energy was consumed by the system to effect a close contact between the rubber and the filler particles, the latter may be assumed to be somewhat loosely connected with the former, and merely filling interspaces in the framework. In the case of carbon black, a filler which when completely wetted by rubber presents a system of high potential energy, mere mixing into the latex did not bring the individual particles to the requisite degree of dispersion.

Summary

1. Interfacial affinity of rubber for fillers is suggested as mainly responsible for the phenomena of tear resistance and resistance to abrasion of vulcanized rubber mixes, whereas "reinforcement," as indicated by increase in tensile strength and resilient energy, is thought to be caused partly by mechanical effects such as friction and thin film formation. Anisotropic fillers are particularly liable to develop such mechanical effects, and thus produce a type of reinforcement which need not necessarily imply increased resistance to wear.

2. Considerable importance is attached to the supposed fibrous network structure of rubber, indicated by recent x-ray work. Gradual destruction of the network during mastication is considered as the cause of the decrease in tear resistance of vulcanized products from overmilled rubber. Similarly the high tear resistance

of latex rubber is explained by assuming the framework unimpaired. The fillers in this case are believed to play a secondary role.

3. The cause of grain effect resides in both the filler and the rubber phase. Isotropic fillers of high affinity for rubber can produce strong grain effect, due to fixation of orientated elementary rubber fibers.

4. The tear resistance and other mechanical properties of a vulcanized rubber compound are functions of the disaggregation of the rubber during milling and mixing, the speed of the accelerator, and the temperature of vulcanization. The best physical properties with any particular compound were obtained when it was either produced direct from latex or by milling in nitrogen. The faster the accelerator employed, and the lower the temperature of vulcanization, the better the physical properties of the vulcanized product.

The author is deeply indebted to F. H. Cotton for his valuable help and assistance, and wishes to record his thanks to T. J. Drakeley for advice given during the course of this investigation. He is also indebted to the Ramsay Memorial Fellowship Trust and the University of Athens for the award of a Fellowship which enabled him to undertake this investigation in England.

The Stress-Strain Relationships of Vulcanized India-Rubber

Part I. The Inflection Point*

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Definition.—The relation between applied load and the resulting extension of vulcanized or unvulcanized rubber may be represented graphically as a curve which is "s" shaped, and there is a point of inflection in the curve. If a load W grams be applied to the rubber, and the resulting length be L , the point of inflection is defined as the point on the curve where the second differential becomes zero and changes sign. More simply, the point of inflection is where the tangent to the curve crosses the curve.

It is well known that the point of inflection exists, but there appears to be no reference in the literature to any attempts to determine precisely its position.

It is also apparent from the many stress-strain curves of rubber which have been published that the point of inflection varies with both the period of cure and the compounding of the rubber.

What follows is an account of some experiments made to investigate the position of the point of inflection in the stress-strain curve of vulcanized rubber.

Preparation of Mixes.—It was decided to carry out experiments on four compounding ingredients, two "inert," namely, whiting and barium sulfate, and two "reënforcing," zinc oxide ("White Seal") and gas black ("Miconex").

The following base mix was employed: rubber (first latex crepe), 100; zinc oxide, 5; stearic acid, 1; sulfur, 2; and accelerator, 1 part by weight.

Master batches were prepared of the uncompounded rubber, and of compounded stock containing 100 parts of filler by weight on the rubber. All master batches were masticated for 15 minutes, and the incorporation of the fillers occupied 25 minutes. These were then blended to form mixes in which the proportions of each filler were 25, 50, 75, and 100 parts by weight on the rubber.

The only variation in the curing agents was in the accelerator, which required modification for the more highly loaded stocks. Preliminary tests, using the hand-tear test as a criterion of cure, were made to ascertain the amount of accelerator necessary for each mix in order to obtain uniform press-cures.

The accelerator used was of the "delayed-action" type, and was suitable for a cure of about 25 minutes at a steam pressure of 25 lb. per sq. in.

After each mixing or blending, a "rest" period of 24 hours was given to secure even sulfur dispersion, and the final mixes were calendered to $1/32$ in. thick, and built up of two plies on the cross to eliminate grain effects.

Vulcanization.—A frame mold was made of $1/16$ -in. mild steel, containing four rectangular spaces 9 in. by 2 in. This permitted four different test-pieces to be vulcanized simultaneously. The four mixes chosen for any one cure in the mold were four which all contained the same filler, but in varying proportions of 25, 50, 75, and 100 per cent. Each mix was vulcanized for periods of 18, 24, and 32 minutes, and these times were chosen as corresponding to "under," "correct," and "overcure," respectively.

* Abstract of thesis submitted to the University of London for the Ph.D. degree

Cutting the Test-Pieces.—Each sample of vulcanized rubber was in turn wrapped in unvulcanized sheet $\frac{1}{16}$ in. thick, on a wooden mandrel. The whole was placed between centers, and by mounting the knife in the slide rest, cuts could be made at $\frac{1}{16}$ -in. intervals.

Marking and Measuring the Test-Pieces.—It was decided to mark each test-piece into thirds, and to measure the elongation of the middle portion. The end portions would then be ample to allow for the so-called "end" effects. It is true that even the middle third of the test-piece, when extended to about 250 per cent elongation, could not be said to have a uniform cross section: it would still have a minimum

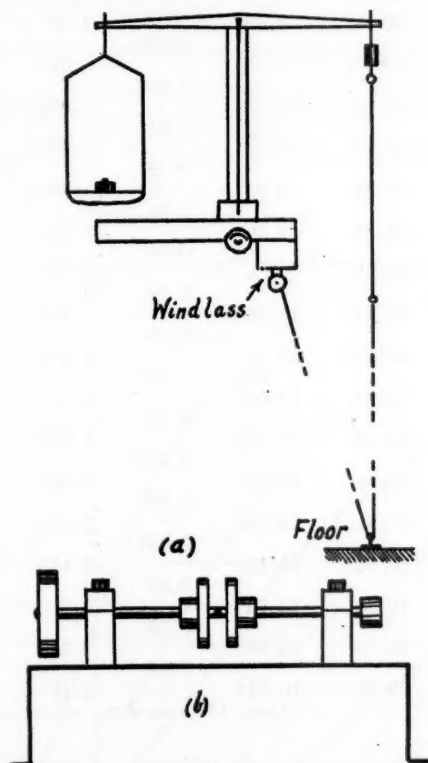


Figure 1

cross section at its center. However, inspection by a low-power microscope showed that the variation over the measured portion was sufficiently small to be neglected.

By a traveling microscope the shorter dimensions of the test-piece were determined to within an error ± 0.0005 cm. Measurements were made at the points marked, and also equidistant between them, and the three readings for each dimension averaged. It is considered that thereby the average area of cross section of the test-piece was determined with an error of less than 1 per cent.

Measurement of Extension under Known Loads.—A chemical balance was removed from the case, and mounted on a firm base. A "windlass" (Fig 1b) was mounted on the underside of the base, in an easily accessible position. The right-hand scale pan of the balance was removed, and a lead weight constructed to re-

place it, such that when a rubber test-piece was mounted ready for extension, the total weight on the right-hand side was equal to that on the left-hand side of the balance (Fig. 1a). This was an approximation for two reasons: (a) The test-pieces varied in density, and hence in mass, and (b) as extension proceeded the tape connecting the specimen to the windlass decreased in length, and therefore in effective mass, as far as the balance was concerned. The maximum error due to these two factors was calculated to be, at an elongation of 250 per cent, 3.5 grams.

TABLE I

w	c	c'	l	dl	L	W	W'
0	100.97	94.04	6.93		1.00	0	0
20	101.08	94.055	7.025	0.095	1.013	10.59	10.73
40	100.91	93.76	7.15	0.125	1.032	21.18	21.85
60	100.63	93.07	7.56	0.41	1.091	31.77	34.65
80	100.37	92.33	8.04	0.48	1.160	42.36	49.05
100	99.86	91.26	8.60	0.56	1.241	52.95	65.7
120	99.35	90.11	9.24	0.64	1.334	63.54	84.7
140	98.87	88.84	10.03	0.79	1.442	74.13	107.0
160	98.395	87.475	10.92	0.89	1.575	84.72	133.5
180	97.825	85.78	12.045	1.125	1.74	95.31	166.5
200	97.315	84.32	12.995	0.95	1.872	105.90	198.0
220	96.86	83.08	13.78	0.785	1.987	116.49	231.5
240	96.435	81.91	14.525	0.745	2.095	127.08	261.2
260	96.09	80.93	15.16	0.635	2.185	137.67	300.7
280	95.61	79.86	15.75	0.59	2.27	148.26	343
300	95.43	79.13	16.30	0.55	2.35	158.85	373
320	95.13	78.39	16.74	0.44	2.41	169.44	409

Area: 1.889 sq. mm.

Readings were taken after mounting the test-piece by placing a 20-gram weight on the pan, releasing the balance beam, and rotating the windlass until the pointer of the balance registered zero. The actual length of the test-piece while under stress was measured by means of a cathetometer, to an accuracy of ± 0.005 cm. Readings were repeated at intervals of 20 grams until the test-piece had been extended past the inflection point.

To illustrate the results obtained, Table I gives the actual readings obtained for a gas black mix containing 75 parts of gas black to 100 parts of rubber, and cured for 18 minutes.

Figure 2 shows the actual load-extension curves for the four gas black mixes, all cured for 18 minutes.

Figure 3 illustrates the method of obtaining the inflection point. The actual load in grams is plotted against dl , and the maximum in the curve gives the in-

flection point. Corresponding values of W and L may then be obtained from the tables.

Symbols Employed.—

- w = actual load in grams,
 c, c' = cathetometer readings,
 l = $c - c'$ = actual length of rubber under test, under a stress of " w " grams,
 dl = difference between values of " l " with successive loads " w ." dl is a measure of the slope,
 L = actual length l under a stress of " W " grams compared with the original length l_0 ,

$$\text{i. e., } L = \frac{l}{l_0}$$

W = stress expressed as grams per sq. mm., based upon the initial area of cross section,

W' = load expressed as grams per sq. mm., based upon the actual area of cross section of the test-piece under a load of W grams,

V = volume of test-piece, assumed constant,

a = area of cross section of test-piece under a load of W grams,

$$\therefore V = La,$$

$$\therefore W' = \frac{W}{a} = \frac{W.L}{L.a} = \frac{W.L}{\text{constant}}$$

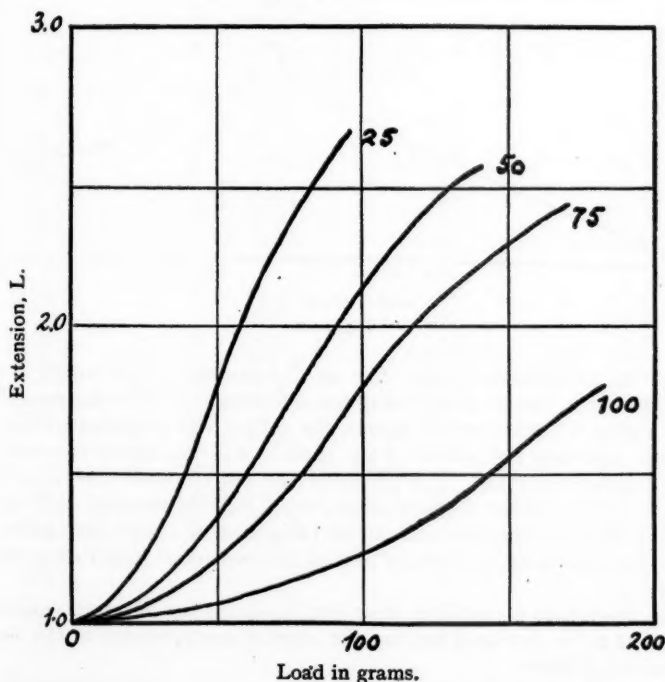


Figure 2

The results were graphed as follows: (1) for each of the 51 test-pieces, L and W were plotted. Figure 2 is an example of the curves obtained. (2) dl and w were plotted to give figures similar to Fig. 3.

The Complication of Creep.—Rubber extended under constant load does not maintain a constant length, but gradually increases in length. This increase is only a

comparatively small fraction of the elongation produced immediately on the application of the load to the rubber, but it takes place gradually over a period of some hours, and finally reaches a limiting value. This phenomenon is known as creep, and has an origin common with that of "sub-permanent" set. Most probably it is concerned with internal flow of the rubber, and is analogous to a viscosity effect.

It is therefore to be expected that in making experiments such as have been described, that creep will be present. The time taken in making each load-extension test varied from 15 to 25 minutes, depending upon the compounding of the rubber.

Creep was observed under the following conditions: (a) At small loads, up to values of 140 to 180 grams, creep was practically non-existent. It was possible to make the cathetometer readings (time 30 to 45 seconds) with the pointer of the balance quite stationary, or at the most moving 1 or 2 divisions. Such motion corresponded to a creep of about 1 mm. on a length of 24 cm. and hence is negligible. (b) At loads greater than those mentioned in (a) creep was noticed, the balance pointer moving comparatively rapidly at first, and then more slowly. During the time taken to read the cathetometer the pointer frequently reached its limit of

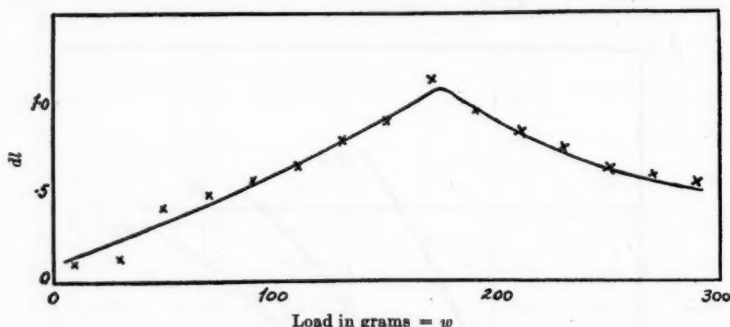


Figure 3

motion. This corresponded to an error up to 4 per cent of the length of the test-piece. Such error due to creep being unavoidable, the following procedure was adopted. After a loading of 140 grams, the rubber was extended to the point of equilibrium, and then the pointer of the balance was held firmly in position while the cathetometer was read. This procedure did not eliminate creep, as the latter is continuous when rubber is under stress, but it enabled readings to be made.

It is to be observed that the load, about 140 grams, at which creep is first noticeable, also corresponds approximately to that at the point of inflection on the stress-strain curve.

Some of the curves for whiting show that the error due to creep caused the inflection point to be displaced beyond the limit of measurement of the apparatus. This is discussed below.

Summary of Results.—For the 51 test-pieces examined, the stress-strain curves were plotted, and all showed a displacement with increasing time of cure and with increasing filler percentage. There was, however, no apparent proportionality between cure or filler percentage (by weight or volume) and the displacement of the curve.

All the curves showed a point of inflection except six, and these were with whiting as a filler. The exceptions were of the longer cures and higher loadings of whiting

mixes. The absence of the point of inflection does not mean that such a point was absent from the stress-strain curve as a whole: it means that creep had entered to such an extent that the inflection point had been displaced beyond the limits of measurement of the apparatus.

The positions of the points of inflection have been read off from curves, and are tabulated below. The accuracy is not high, but is sufficient to show how the inflection point changes with cure and filler percentage.

TABLE II			
Per Cent	Cure 18 Min.	24 Min.	32 Min.
	<i>Base Mix</i>		
	W = 56 g.	58 g.	78 g.
	L = 240%	172%	228%
	<i>Whiting</i>		
25	W = 57 g.	86.5 g.
	L = 218%	209%
50	W = 70 g.
	L = 194%
75	W = 72 g.	98 g.
	L = 183%	193%
100	W = 79 g.
	L = 179%
	<i>Barium Sulfate</i>		
25	W = 49 g.	65 g.	71 g.
	L = 215%	224%	198%
50	W = 53.5 g.	67 g.	73 g.
	L = 205%	198%	182%
75	W = 57 g.	73 g.	76 g.
	L = 186%	190%	172%
100	W = 57 g.	75 g.	76 g.
	L = 168%	173%	169%
	<i>Zinc Oxide</i>		
25	W = 60 g.	61 g.	57 g.
	L = 228%	208%	205%
50	W = 65 g.	69 g.	64 g.
	L = 204%	207%	172%
75	W = 63 g.	71 g.	83.5 g.
	L = 187%	208%	197%
100	W = 68 g.	73 g.	86 g.
	L = 189%	180%	178%
	<i>Gas Black</i>		
25	W = 46 g.	61 g.	82 g.
	L = 168%	164%	165%
50	W = 79 g.	85.5 g.	80 g.
	L = 180%	165%	151%
75	W = 92 g.	95 g.	125 g.
	L = 165%	162%	153%
100	W = 137 g.	195 g.	197 g.
	L = 145%	161%	153%

Discussion of Results.—The measurement of the points of inflection for the samples of rubber examined offer but little in the way of general inferences. This is undoubtedly due to the method of determination. As may be seen from Table II, the individual values of dl are subject to a comparatively large error, in which creep must play some part. Further, it is only possible to read approximately the maxima on curves of the type of Fig. 3.

The values of load and elongation at the point of inflection, Table II, show that:

(1) The point of inflection varies with time or cure, filler, and percentage of filler. This disagrees with the conclusion of Ariano (*India Rubber J.*, 72, 272 (1926)), who states that the point of inflection is always approximately at an extension of 100 per cent. (2) The load required to reach the point of inflection increases with the percentage of filler and with the time of cure. Except with gas black as a filler, the value of this load is nearly always between 50 and 80 grams. (3) The elongation required to reach the point of inflection decreases with percentage of filler and with time of cure. A remarkable exception to this is the barium sulfate mixes, cured for 24 minutes. The elongations to reach the inflection point are in three of the four specimens, higher than the corresponding figure for the 18 minutes and the 32 minutes cure, respectively. (4) The gas black mixes show considerable divergence from (2) and (3). Whereas the other three fillers show compara-

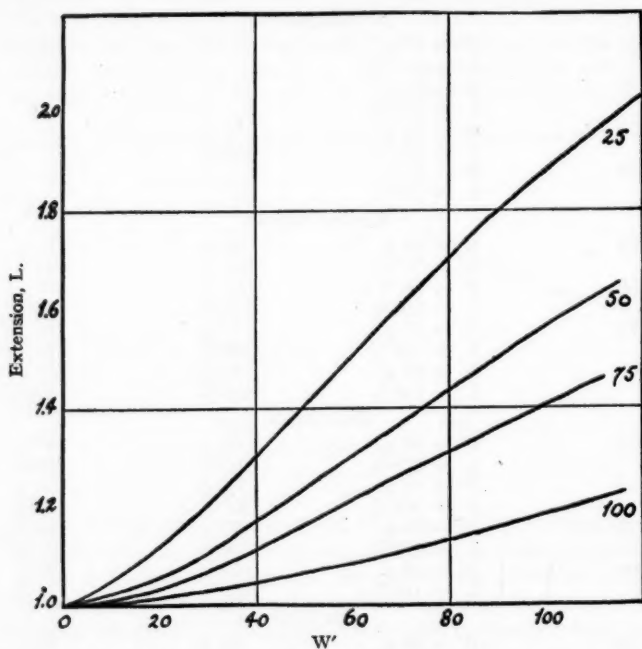


Figure 4

tively small variation in the load, and a fairly wide variation in the elongations required to reach the inflection point, the corresponding figures for gas black show extremes of 180 and 145 per cent elongation, and the load varies between 46 and 197 grams.

Undoubtedly the elongation data are complicated by volume changes, except perhaps those for gas black, which suffer only a very small volume change under extension (Ariano, *loc. cit.*).

The Hatschek Correction.—Hatschek (*J. Soc. Chem. Ind.*, 40, 251T (1921)), showed that by correcting for the diminution in area of cross section of the test-piece, during extension, the point of inflection disappeared. After this correction, the stress-strain curve gave good agreement with the conchoidal curve suggested by Schidrowitz and Goldborough (*J. Soc. Chem. Ind.*, 38, 347T (1919)).

The accuracy of the results given in the present paper appear to warrant an examination of the stress-strain curve, with the Hatschek correction applied.

On the assumption that the volume of the rubber remains constant during extension, curves relating percentage elongation and load in grams per sq. mm. of actual cross section may be obtained by plotting W' and L . The derivation of W' is given on page 489. Figure 4 shows the plotting of W' and L for the four gas black mixes whose actual curves for load and extension are given in Fig. 2. Only the first portion of the data for each curve has been plotted. The reasons are that if the Hatschek correction be valid, the whole curve (W'/L) will be concave toward the load axis, and if the point of inflection be still apparent in the curve, its earlier portion will be convex, and the later portion only will be concave to the load axis.

Hence any divergence from the Hatschek correction will be completely demon-

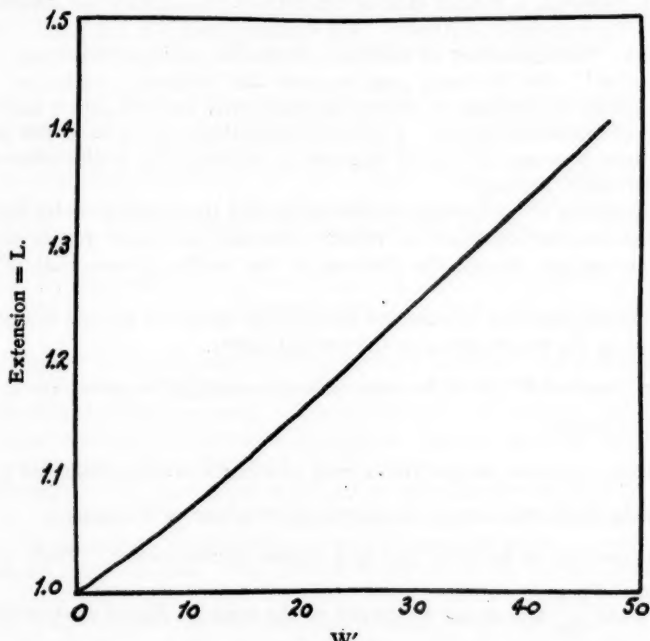


Figure 5

strated by the earlier portion of a stress-strain curve (W'/L) being convex toward the load axis.

In Figure 5 is plotted the corrected curve for uncompounded rubber, cured for 24 minutes. With all the 51 samples examined, the plotting of W' and L showed, without exception, a slight convexity of the curve in its earlier stages toward the load axis. Figures 4 and 5 are examples of such curves. Though the curvature is slight, yet it must be borne in mind that for such curves to be straight, the values of L would have to be different by 5 to 10 per cent, whereas the measurements of L and of a are accurate to less than 1 per cent.

The inference may therefore be drawn that the correction for reduction in cross-sectional area of rubber under stress does not eliminate the point of inflection in the stress-strain curve, though the curves approximate closely to the form suggested by Hatschek.

The Effect of Volume Change during Extension of Rubber upon the Shape of the Corrected Curve (W'/L).—The corrected curve makes no allowance for any change in volume of the rubber during its extension. Such changes undoubtedly do occur, as is shown by the experiments of Schippel (*J. Ind. Eng. Chem.*, **12**, 33 (1920)), and of Ariano (*India Rubber J.*, **72**, 271 (1926); **75**, 759 (1928)).

Whereas Schippel (*loc. cit.*) measured only the volume increase at various percentages of elongation for several compounded rubbers, Ariano dealt with the subject in more detail. He measured simultaneously the length and area of cross section of test-pieces of compounded rubber at various stages of elongation, and hence concluded that the Hatschek correction produced a curve having no inflection point. He suggested that all curves, based upon the actual area of cross section of the rubber, were rectangular hyperbolae.

There is, however, a certain lack of consistency in some of the statements attributed by the translator to Ariano. For example (*ibid.*, **75**, 759 (1928)) the statement occurs: "the constancy of volume . . . holds for mixings containing only rubber and sulfur." On the same page appears the following conclusion: "For a given ingredient the increase in volume increases with the elongation and with the proportion of ingredient added. For small elongations (up to 50 or 100 per cent), however, there is generally a small decrease in volume; this is also observed with pure rubber-sulfur mixings."

His examination of compounded rubbers showed that, undoubtedly with about one-half the samples examined, a volume decrease did occur during the earlier stages of elongation, though the diagram of the results is somewhat difficult to follow.

It is therefore necessary to examine the possible effects of volume change during extension upon the results given in the present paper.

Plotting L against W' ($= WL$) is equivalent to plotting L against $\frac{LW}{La}$ as $La = V$ (assumed constant).

Were there a volume change, the correct plotting would be L against $\frac{LW}{La(1 \pm x)}$ where x is the fractional change in volume under a load of W grams.

(1) Assume x to be positive, that is, a volume increase occur. Then $\frac{LW}{La(1+x)}$ is smaller than $\frac{LW}{La}$ and as far as graphs of the type of Fig. 4 are concerned, the convexity toward the load axis is accentuated.

(2) Assume x to be negative, that is a volume decrease occur. Then $\frac{LW}{La(1-x)}$ is greater than $\frac{LW}{La}$ and graphs of Fig. 4 type tend to be straightened out.

The point arises whether this decrease in volume, which Ariano notes as occurring in the first 100 per cent extension, tends to eliminate the point of inflection.

The results of Ariano, however, show that for some 20 compounded rubbers which he examined, about one-half of these show a volume decrease below 100 per cent extension, and the remainder increase their volume continuously during the whole extension.

Hence it is impossible for such volume decrease to eliminate the point of inflection from all 51 graphs the author obtained.

Further, Fig. 5 shows for uncompounded rubber the deviation of the corrected

curve from a straight line. For these results to agree with the conclusions of Hatschek and of Ariano, the points on the curves would have to be displaced in many cases by 5 per cent, and in some cases by 10 per cent. Therefore, the volume decrease in the earlier stages of elongation may influence, but cannot eliminate, the slight convexity which the graph in Fig. 5 shows toward the load axis.

Conclusion.—The correction for reduction in cross sectional area of rubber undergoing extension, suggested by Hatschek, though closely approximating the resulting curve for load and extension to a conchoidal form, does not eliminate the point of inflection.

The point of inflection is therefore an inherent property of the stress-strain curve of rubber.

The author thanks T. J. Drakeley for advice during the course of the investigation.

Part II. Elasticity and Structure

In Part I of this work, it has been shown that the point of inflection is inherent in the stress-strain curve of vulcanized rubber. In the present paper an attempt is made to account for the presence of the inflection point.

Mathematical Representation of the Stress-Strain Curve.—The early attempts at a mathematical formulation of the stress-strain curve are summarized by Ariano (*India Rubber J.*, **72**, 271 (1926)) who suggested the equation of a hyperbola to be applicable.

In 1930, Kröger and Möbius (*Gummi Ztg.*, **44**, 1153, 1209 (1930)) applied various mathematical series to the curves, but found fair agreement only at higher elongations.

It is apparent from a survey of the literature cited that in no instance is a satisfactory formulation of the stress-strain curve of rubber obtained, particularly with regard to the inflection point. The reason is not far to seek. All the investigators have considered rubber as a continuum, thereby omitting to allow for any structural changes during distortion of the rubber.

Gel Structure.—The unit of gel structure is undoubtedly the fibril or long chain molecule. As is shown by the work of many investigators, the fibril accounts satisfactorily for several of the properties shown by natural products such as rubber, gelatin, hair, and cellulose. The important papers of W. Haller (*Kolloid-Z.*, **56**, 3, 257 (1931); **61**, 1, 26 (1932)), elucidate further the behavior of lyophil colloids. Assuming that the fibrils are flexible, free rotation occurring about the single valences uniting adjacent links of the fibrils, Haller discussed the results of the constrained Brownian motion of the links. The thermal motion causes the fibrils to adopt a "snake-like" form, and upon this basis, Haller explained with marked success, the osmotic and swelling pressures of lyophil colloids. He also deduced a viscosity equation closely resembling those obtained experimentally by other investigators.

The evidence for fibril structure of rubber, gelatin, etc., has been summarized by K. Meyer, von Susich and Valko (*Kolloid Z.*, **49**, 208 (1932)).

A gel may be regarded as a material composed of fibrils which, being highly flexible, and having no ordered arrangement, are therefore entangled. Such an entanglement must cause a considerable opposition to the removal of any one fibril by virtue of the friction with adjacent fibrils. Further the presence of polar groups in the fibrils results in these groups binding themselves together by what is known as, for want of a precise definition, "residual affinity." If also, as will be shown later, some chemical combination be possible between the fibrils at various points

along their length, a "three-dimensional network" is thereby completed. Such a structure is still highly deformable, either by mechanical force or by swelling with a suitable solvent.

Poole (*Trans. Faraday Soc.*, **21**, 114 (1925); **22**, 82 (1926)) has developed in considerable detail the fibril structure for gelatin gels, and Hermann and Gerngross (*Kautschuk*, **8**, 181 (1932)) have applied a fibril network structure to explain x-ray diffraction phenomena in rubber.

The high reversible extensibility of rubber and gelatin must be attributed either to the unfolding of fibrils which tend to coil up (a coil being presumably the condition of minimum free energy), or more probably to the straightening out of a fibril which tends to contract under constrained Brownian motion of its links. Certainly some such change of fibril form must be possible. This was emphasized by Astbury (*Trans. Faraday Soc.*, **29**, 193 (1933)), while Adam (*ibid.*, p. 90) also concluded from measurements upon surface films of cellulose derivatives that fibrils are flexible.

Some distinction must be drawn between reversible gels such as a gelatin-water gel, and irreversible gels such as vulcanized rubber. In the former a return to the sol state is possible by a rise in temperature. The linkages between the polar groups of adjacent fibrils become relatively weaker with rise of temperature and finally so weak that internal network structure disappears, and a sol results. If, however, the sol be treated with formaldehyde, gelling is irreversible, indicating a much stronger inter-fibrillar union. The latter is analogous to vulcanized rubber, wherein the union of fibrils occurs by chemical means under the influence of sulfur.

Vulcanized oils offer confirmatory evidence for the production of a three-dimensional network during gelation. The action of sulfur chloride upon ethyl oleate is to form merely a liquid of viscosity somewhat higher than that of the parent substance. Using glycol dioleate, a liquid of still higher viscosity is obtained, but again no signs of gel formation may be observed. With, however, glycerol trioleate, the familiar white substitute or factice is produced, which is an elastic substance. Such results are explained as follows. Each oleic acid chain carries one double bond, which is attacked by the sulfur chloride, and which forms a point of union with another acid chain. With ethyl oleate, union can occur only between two molecules, each possessing one point of linkage. Each molecule of glycol dioleate possesses two double bonds, and hence the action of sulfur chloride is to produce, by the union of single molecules, double bond to double bond, a long chain. This formation is indicated by the high viscosity of the product.

With glycerol trioleate, however, in addition to the two double bonds necessary for the formation of fibrils, there is a third double bond which permits of inter-fibrillar linkage. A network structure is thereby formed.

Such a mechanism of gel formation may be confirmed by reacting upon oleyl chloride with the theoretical amount of sulfur chloride necessary to unite the oleyl chloride chains. Heat is produced and a dark brown viscous material is formed. When cool, the addition of the theoretical quantity of glycerol for esterification causes no action in the cold, but on heating to about 120° C., hydrochloric acid is evolved, and the liquid sets to a gel.

Such experiments as described above confirm the production of a network structure in a gel. Comparatively simple molecules, of known structure are employed, and though most probably the vulcanization of rubber occurs in a similar manner, rubber is a natural product far more complex than an ester of oleic acid. Hence the elucidation of the problem of vulcanization of rubber is more difficult.

The Stress-Strain Curve for Vulcanized Rubber.—On the basis of a three-dimen-

sional network structure, composed of interlocked flexible fibrils, the following explanation is put forward to account for the point of inflection on the stress-strain curve and also for the slight volume change which occurs during extension.

Highly elastic organic substances, *e. g.*, rubber, may be regarded as being composed of flexible fibrils, which are: (i) very long compared with their cross sectional area, (ii) intermingled in a completely disordered fashion, (iii) linked at the points where they meet, (iv) elastic by virtue of a change of form.

As a consequence of the above, it follows that the fibrils form a three-dimensional network, and the system as a whole is highly elastic.

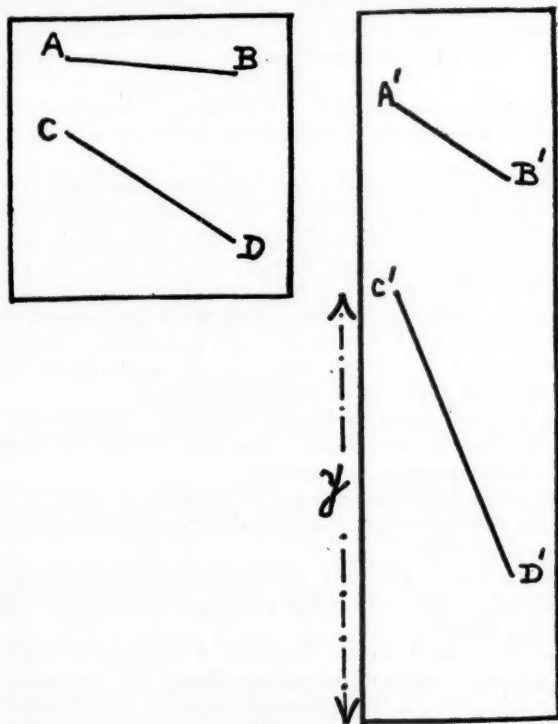


Figure 1

The shape of a fibril being very irregular, for the purpose of the discussion which follows, a fibril is represented by a straight line, joining its points of linkage to two other fibrils. The length of this line is called the effective length of the fibril.

Behavior of Individual Fibrils When an Elastic System Is Distorted.—Consider a cylinder of material which contains n fibrils, n being sufficiently large for statistical treatment. The cylinder is extended in a direction parallel to its axis, a distance y , by a load p .

According to their positions relative to the direction of extension of the cylinder, different fibrils will show, under the extension y , different behavior.

This is illustrated by considering two fibrils, before and after a finite extension of the cylinder.

In Fig. 1 fibril AB (length = l_0) lies at an angle of nearly 90° to the axis of the

cylinder. Fibril CD (length = l_0) lies at an angle of about 45° to the same direction. On extending the cylinder a finite distance y , the two fibrils behave in different ways. Figure 1 shows that $A'B'$ is less in length than AB , i. e., the fibril has become compressed while CD has extended to $C'D'$. The reason for this behavior is that the fibrils of the system form a three-dimensional network whereby each fibril must always retain its position relative to all other fibrils, no matter how the solid is distorted.

An extension y means a corresponding reduction in cross sectional area of the cylinder. Hence two effects are to be observed as acting upon any fibril when the cylinder is extended. These effects are: (i) an extending effect, which is proportional to the extension of the cylinder y , (ii) a compressive effect, which reduces the effective length. This effect is proportional to the reduction in diameter of the cylinder.

Which of these effects predominates in the change of length of a fibril when the cylinder is extended depends upon the angle at which the fibril lies to the cylinder axis.

Further, in the unextended cylinder there is a critical angle ϕ_c to the axis. Fibrils in the network which lie inside the angle ϕ_c will, on extension of the cylinder, merely be extended. Those fibrils lying outside the angle ϕ_c will first be compressed.

Such compression cannot continue indefinitely with continual extension of the cylinder, because the angle which any fibril makes with the axis of the cylinder is always diminishing. Hence, most of the fibrils which are initially subject to compression, sooner or later reach a point at which compression ceases and extension commences. This point is decided solely by the angle which the fibril bears initially to the axis, and must also be the critical angle ϕ_c .

This may all be summarized by saying that fibrils lying outside the angle ϕ_c , will, on extension of the cylinder, sooner or later pass through this angle, and, at the same instant, from compression to extension.

The extent to which the cylinder must be extended in order to bring any particular fibril to the critical position obviously depends upon its angle to the cylinder axis in the unstretched state.

A very small fraction of the fibrils will undoubtedly lie at right angles to the axis of the cylinder. These will suffer continual compression only, no matter what the value of y may be.

Calculation of the Critical Angle.—Consider a cylinder of vulcanized rubber, which, for the purpose of eliminating surface effects, may be inside a larger piece of rubber. It consists of a three-dimensional network, and contains n fibrils each of average length, l_0 . n is sufficiently large for statistical treatment. Let the cylinder of rubber be extended a fraction, y , of its length in the axial direction. For any fibril in the cylinder the following conditions hold before and after extension:

	Before	After
Length of cylinder.....	1	$1 + y$
Length of fibril.....	l_0	l_w
Angle of fibril to axis of extension.....	ϕ_0	ϕ
Longitudinal projection of ditto.....	$l_0 \cos \phi_0$	$l_w \cos \phi$
Transverse projection of ditto.....	$l_0 \sin \phi_0$	$l_w \sin \phi$

Consider the volume of the rubber to be constant during extension:

$$\begin{aligned} \therefore l_w \cos \phi &= (1 + y) l_0 \cos \phi_0 \\ l_w \sin \phi &= (1 + y)^{-1/2} l_0 \sin \phi_0 \\ \therefore l_w^2 &= l_0^2 (1 + y)^2 \cos^2 \phi_0 + l_0^2 \frac{\sin^2 \phi_0}{1 + y} \end{aligned}$$

At the critical angle the effective length is a minimum.

$$\therefore \frac{dl}{dy} = 0 = 2(1+y)l_0^2 \cos^2 \phi_0 - l_0^2 \frac{\sin^2 \phi_0}{(1+y)^2}$$

Whence $\tan \phi_0 = \sqrt{2}(1+y)^{1/2}$.

If in the unextended rubber, a fibril happens to be at the critical angle, then $y = 0$, and

$$\phi_c = \phi_0 = \tan^{-1} \sqrt{2} = 54.5^\circ.$$

All fibrils lying in the unextended rubber at an angle ϕ_0 which is greater than ϕ_c require an extension of the rubber (thus compressing the fibril) to bring them to the critical angle.

$$\begin{aligned} \therefore \tan \phi_c &= \frac{l_0 \sin \phi_0}{\sqrt{1+y}} \div l_0 \cos \phi_0 (1+y) \\ &= \tan \phi_0 (1+y)^{-3/2} \text{ and } \phi_c = 54.5^\circ. \end{aligned}$$

The Storing of Energy during Extension.—The compression of some of the fibrils during extension of an elastic material results in energy being stored. With further extension of the material, some of the compressed fibrils will pass through the critical angle, and then will be extended. No energy is required to extend them. On the contrary, the potential energy already acquired during their compression will serve to make the extension of the material as a whole easier.

The effect of this energy change upon the stress-strain curve of the material may be deduced.

The number of fibrils undergoing compression rapidly decreases as the material is extended. The energy stored up, however, by any individual fibril is dependent upon the distance the material must be extended to bring the fibril to the critical angle.

The stress-strain curve of the material therefore falls naturally into three stages: (a) The first stage, where many fibrils are being compressed. Here energy is absorbed both in compressing some fibrils and in extending others. (b) The second stage, where the majority of the fibrils undergoing compression in (a) are passing from compression to extension. The energy of compression is being given out, and extension of the material as a whole is easier. (c) The third stage, where practically all fibrils are now subject to true extension, for which energy must be supplied.

These three stages are to be observed in the stress-strain curve of rubber, the second stage containing the point of inflection.

The results of Ariano (*loc. cit.*) are in agreement with the theory that compression of some fibrils occurs during extension of the material. He noted for pure rubber-sulfur mixes (as well as for compounded rubbers) a small decrease in volume during the first 100 per cent of extension of rubber. The Joule effect was also in accordance with the result; a decrease in temperature of the rubber was noted over the same range of extension, and then, with subsequent further extension, a rise in temperature occurred.

An equation expressing the whole course of the stress-strain curve of rubber is at present difficult to obtain. The elastic behavior of a finite mass of rubber is dependent upon at least two factors: (1) the elasticity of the individual fibrils, (2) the behavior under distortion of a three-dimensional network of fibrils.

In the present paper, some attempt is made to deal with (2). For the solution of (1) however, assuming Haller's conception of restricted Brownian motion of the fibrils, a reasonably accurate value of the length of a fibril is required. While

numerous very approximate estimations of this length have appeared from time to time in the literature, all the results have been obtained for unvulcanized rubber. There is at present no means of estimating the length of a fibril in vulcanized rubber, and until this be obtained, the elasticity of the individual fibril cannot be calculated.

Deduction of the Stress-Strain Equation.—If Hooke's law be assumed for an individual fibril, the energy absorbed for the extension of one fibril from initial length l_0 to final length l_w is

$$W = \frac{\lambda}{2} (l_w - l_0)^2$$

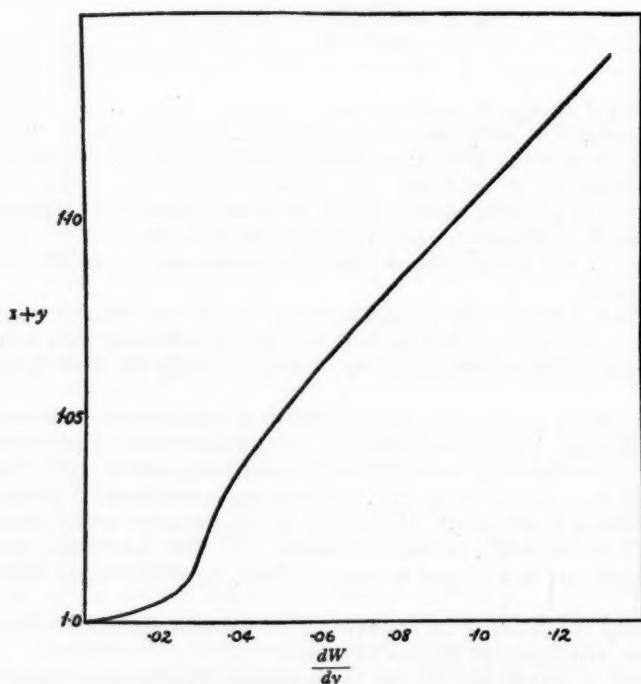


Figure 2

where λ is the coefficient of elasticity for the fibril.

There is random distribution of fibrils in the unstretched rubber.

\therefore For n fibrils, for values of ϕ between $\pi/2$ and 0, the energy absorbed

$$\begin{aligned} W &= \int_0^{\pi/2} n \cdot w \cdot \cos \phi \cdot d\phi \\ &= \frac{n\lambda}{2} \int_0^{\pi/2} (l_w - l_0)^2 \cos \phi \cdot d\phi. \end{aligned}$$

Put $\sin \phi = t$, and expand.

$$W = \frac{n\lambda}{2} \int_0^1 \left[(1+y)^2 (1-t^2) l_0^2 + \frac{l_0^2 t^2}{1+y} + l_0^2 \right. \\ \left. - 2 \sqrt{(1+y)^2 (1-t^2) l_0^2 + \frac{l_0^2 t^2}{1+y} \cdot l_0} \right] dt.$$

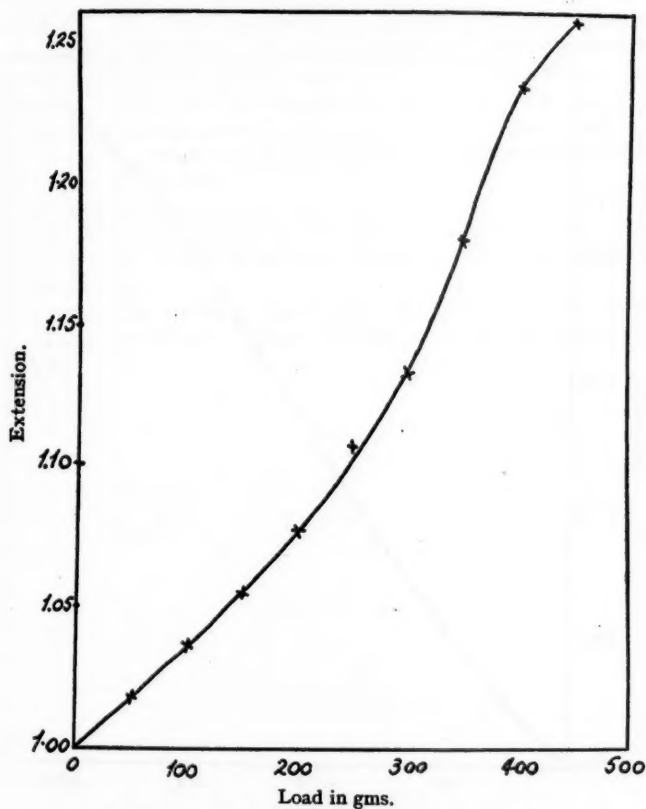


Figure 3—Stress-Strain Diagram for Gelatin Gel

Integrating

$$W = \frac{n\lambda l_0^2}{2} \left[\frac{2}{3} \cdot (1+y)^3 + \frac{1}{3} \cdot \frac{1}{1+y} - \sqrt{1+y} + 1 \right. \\ \left. - \sqrt{1 - \frac{1}{(1+y)^3}} \sin^{-1} \sqrt{1 - \frac{1}{(1+y)^3}} \right].$$

W being the energy absorption during the extension of the rubber, the load at any elongation is given by $\frac{dW}{dy}$.

$$\frac{dW}{dy} = \frac{n\lambda l_0^2}{2} \left[\frac{4}{3} \cdot (1+y) - \frac{1}{3} \frac{1}{(1+y)^2} + \frac{1}{2} \frac{1}{(1+y)^{3/2}} \right. \\ \left. - \sin^{-1} \sqrt{1 - \frac{1}{(1+y)^3}} \left\{ \sqrt{1 - \frac{1}{(1+y)^3}} \right. \right. \\ \left. \left. - \frac{3}{2} \cdot \frac{1}{\left(1 - \frac{1}{(1+y)^3}\right)^{3/2} (1+y)^3} \right\} - \frac{3}{2} \cdot \frac{1}{\left(1 - \frac{1}{(1+y)^3}\right) (1+y)^{3/2}} \right]$$

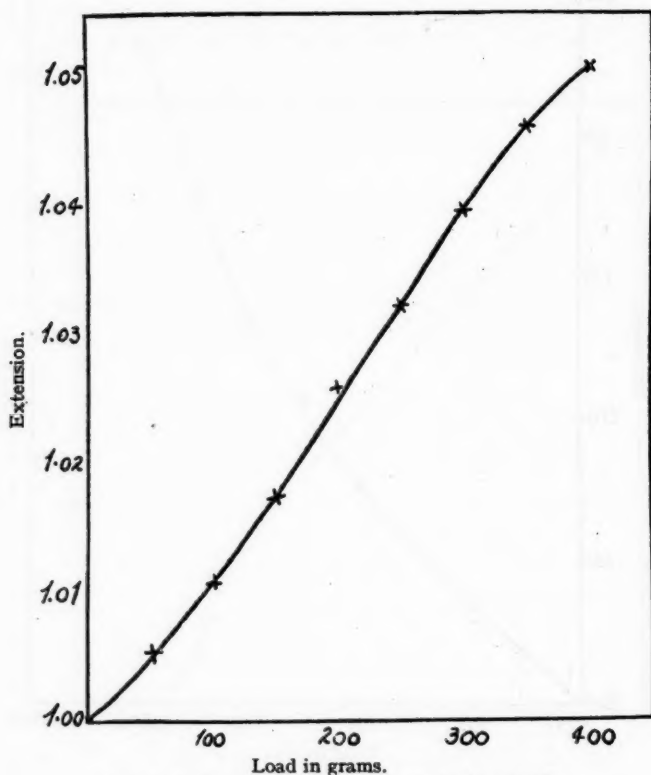


Figure 4—Stress-Strain Diagram for Vulcanized Oil

Plotting $\frac{dW}{dy}$ against y will produce a graph of the relation between load and extension of the elastic material. The result is shown in Fig. 2.

The following points are to be noted in the examination of the curve.

In the comparison with an actual stress-strain curve of rubber, the latter must be one in which the correction for reduction in cross sectional area with extension has been applied. On the assumption of the absence of all plastic flow in the rubber, the number of fibrils passing through a plane in the test-piece normal to the direction of extension is the same whether the extension be small or large. The more accurate stress-strain curve for rubber is therefore that in which the correction, first suggested by Hatschek, is included.

Under these conditions the theoretical inflection point is at 2 to 3 per cent extension, while in practice it appears between 20 to 40 per cent. The agreement is as good as can be expected in view of the approximate nature of the mathematical deduction, and the neglect of plastic flow.

The equation suggests that the point of inflection is independent of the average length of a fibril, l_0 . The second differential, equated to zero, will give a value for y independent of l_0 .

In the deduction of the stress-strain equation, no specific chemical formula has been assumed. The fibril structure is representative of several substances differing widely in chemical properties. It therefore follows that all elastic gels which show high reversible extensibility should also show, in their stress-strain curves, a point of inflection. Two provisional experiments have been made, one for a vulcanized oil, and one for a gelatin-glycerol-water gel. The extensions were read to ± 0.0005 cm. and the results are given in Figs. 3 and 4. In both diagrams the curves appear to show a point of inflection.

It is also of interest to observe the stress-strain curves for cellophanes given by van Iterson (Discussion following the communication of Mark, *Trans. Faraday Soc.*, 29, 6 (1933)). Both curves show a marked point of inflection at extensions of 10 to 20 per cent.

In conclusion, the author acknowledges with gratitude, the assistance of Professor G. Temple, of King's College, London, in the mathematical development of the problem.

The Stress-Strain Relationships of Vulcanized India-Rubber: A Correction

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In the preceding paper a theoretical stress-strain curve for a material composed of a random three-dimensional network of elastic fibrils was deduced.

Owing to an error in the mathematical treatment of the problem, the equation representing the relation between load (dW/dy) and elongation (y) is incorrect, and hence also the curve in Fig. 1 representing this relation is incorrect in shape.

The equation should read

$$W = \int_0^{\pi/2} n w \cdot \sin \phi_0 \cdot d\phi_0$$

where

- W = work done in stretching a mass of the material;
- n = number of fibrils in the mass;
- w = work done in stretching one fibril;
- ϕ_0 = the angle (before stretching) between the direction of a fibril and the direction of stretching.

By continuing the calculation as in the preceding paper the following is obtained:

$$W = \frac{n\lambda l_0^2}{2} \left[\frac{L^2}{3} - L + 1 + \frac{2}{3L} + \frac{\log_e(L^{3/2} - \sqrt{L^3 - 1})}{\sqrt{L^4 - L}} \right] \quad (1)$$

where

- λ = force required to produce unit extension in a fibril of initial length l_0 ;
- $L = 1 + y$ = ratio of stretched length to initial length of the mass of material.

Now $\lambda = mx/l_0$, where m = the effective elastic modulus (Young's modulus) of a fibril, and x = the effective cross section of a fibril. Let v = volume of the mass of material under test; then $v = nxl_0$, so that in equation (1) the expression $n\lambda l_0^2$ becomes mv .

Consider now a unit cube of the material ($v = 1$), and let F = force required to extend this to length L ($= 1 + y$). Then $F = dW/dL$ and hence from equation (1):

$$F = \frac{m}{2} \left[\frac{2L}{3} - \frac{2}{3L^2} - 1 - \frac{3}{2(L^3 - 1)} - \frac{(4L^3 - 1)\log_e(L^{3/2} - \sqrt{L^3 - 1})}{2(L^4 - L)^{3/2}} \right] \quad (2)$$

Values of F corresponding to various values of L are given in the following table which includes also the slope of the load-elongation curve (dF/dL).

$L (= 1 + v)$	F	dF/dL
1.00	0	
1.02	$0.00397 \times m$	$0.1985 \times m$
1.05	0.00982	0.1950
1.10	0.01946	0.1928
1.15	0.02908	0.1923
1.20	0.03878	0.1940
1.40	0.07972	0.2092
1.60	0.12506	0.2286
1.80	0.17463	0.2480
2.00	0.22770	0.2654
2.20	0.28360	0.2794
2.40	0.34167	0.2904
2.60	0.40144	0.2988
2.80	0.46254	0.3056
3.00	0.52467	0.3106
3.40	0.65120	0.3164
3.80	0.77985	0.3216

The values for dF/dL show that the load-elongation curve is initially concave to the elongation axis, but the curve inflects at about 11 per cent elongation (see figure), beyond which it is convex to this axis. There is no other point of inflection below 280 per cent elongation.

When the load-elongation curve is drawn, the inflection is found to be barely perceptible. While, therefore, the network structure suggested for vulcanized

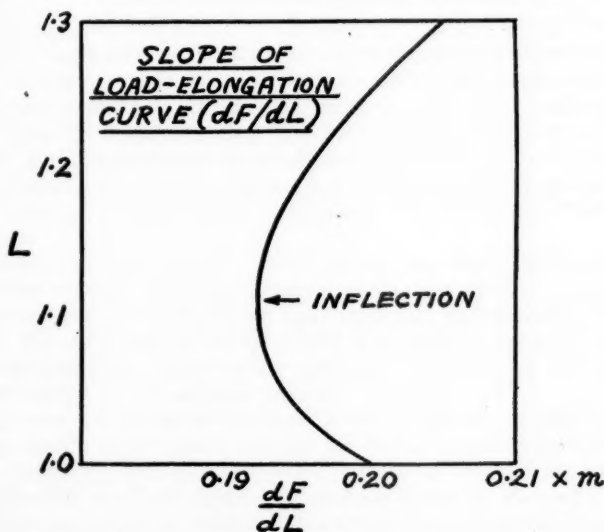


Figure 1

rubber, gelatin, and vulcanized oils (Shacklock, *loc. cit.*) offers some explanation for the inflection point, it appears that this explanation alone is insufficient for the pronounced inflection observed in experiment. The behavior of an individual fibril under stretching is at present quite unknown, and hence the assumption of Hooke's Law, though at this stage necessary, is most probably incorrect. Further, the equation takes no account of interfibrillar friction Mark (*Trans. Faraday Soc.*,

29, 6 (1933)), a factor which must play a prominent part in the extension of gels.

It can be shown that when the elongation y is infinitesimal, equation (2) becomes,

$$F = \frac{my}{5}$$

The elastic modulus of the material for infinitesimal extensions is thus one-fifth of the modulus of the individual fibrils.

Similarly, when y is very large, equation (2) approaches the limiting form:

$$F = \frac{my}{3}$$

The modulus of the material thus approaches a value equal to one-third of the modulus of the fibrils as the elongation increases.

It may be noted that the absence of the term l_0 in equation (2) confirms the conclusion previously drawn (Shacklock, *loc. cit.*) that in a material having the structure assumed, the position of the point of inflection on the load-elongation curve is independent of the length of the fibrils.



Studies on the Nature of the Action of Organic Accelerators for Rubber Vulcanization

IV. The Detection and Analysis of Organic Accelerators. Systematic Identification of Organic Accelerators

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Though much work has been carried out and recorded on the comparative vulcanizing power of various organic accelerators, yet so far as the author is aware, there is very little published work on the detection of commercial organic accelerators; probably a few laboratories have some special test of their own, but as yet no one has seriously taken up this field.

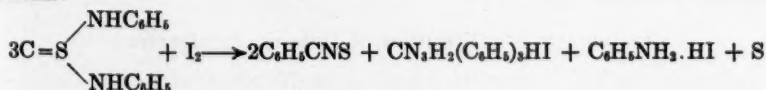
The present investigation was carried out with a view to devise a simple but satisfactory systematic method of identifying general organic accelerators now used in the rubber industry.

Color Reactions of Organic Accelerators

Some years ago, Wistinghausen (*Kautschuk*, 5, 77 (1929)) called attention to the formation of colored complex compounds of several organic accelerators with cobalt salts of unsaturated organic acids. After some preliminary researches, the present author has tried to make use of this color reaction as a means of identifying general organic accelerators systematically. Careful tests were conducted on over thirty accelerators of different kinds by dissolving about 0.05 g. of the accelerators in question in benzene (or benzene-alcohol) in a test tube and adding a few drops of a 1 per cent solution of cobalt oleate in benzene. The following interesting results were obtained.

From the above results it will be seen that the majority of the organic accelerators give color reactions with cobalt oleate, so that cobalt oleate appears to have distinct possibilities as a reagent for the systematic identification of organic accelerators. The only problem to be solved is to devise a suitable method of detecting several exceptional accelerators which give no coloration with cobalt oleate. The present author has solved this problem as follows.

(1) *Thioureas*.—Thiocarbanilide may be recognized by its characteristic odor, which is noticeable when heated, but this method of detection seems to be unreliable. The author has devised a new sensitive method of identifying thiocarbanilide by the application of cobalt oleate. It has been shown by Rudneff (*Ber.*, 11, 987 (1879)) that when iodine is dissolved in a solution of thiocarbanilide in benzene, products such as phenyl mustard oil, sulfur and hydrogen iodide-addition compounds of triphenylguanidine and aniline are obtained according to the following formula:



The author has found that besides the above reaction, a part of phenyl mustard oil reacts with sulfur and is converted to mercaptobenzothiazole. Thus a solu-

tion of thiocarbanilide in benzene with a small amount of iodine dissolved will immediately give an intense greenish blue coloration from mercaptobenzothiazole on adding a few drops of cobalt oleate solution in benzene. Di-*o*-tolylthiourea and di-*p*-tolylthiourea can also be identified in a similar way as in the case of thiocarbanilide.

(2) *Tetramethylthiouram Disulfide and Dibenzothiazole Disulfide*.—In the presence of zinc dust and dilute hydrochloric acid, tetramethylthiouram disulfide and dibenzothiazole disulfide are reduced to dimethylamine dimethyldithiocarbamate

TABLE I—Color Reactions of Organic Accelerators

Accelerator	Color Developed
(1) Aldehyde-ammonia condensation products	
Hexamethylentetramine	Grayish violet with tinge of green
Acetaldehyde-ammonia	Nil
(2) Aldehyde-amines	
Methylene-aniline	Nil
Methylene- <i>p</i> -toluidine	Nil
(3) Thioureas	
Thiocarbanilide	Nil
Di- <i>o</i> -tolylthiourea	Nil
Di- <i>p</i> -tolylthiourea	Nil
(4) Guanidines	
Diphenylguanidine	Purple
Di- <i>o</i> -tolylguanidine	Purple
Triphenylguanidine	Slightly purple
Phenyl- <i>o</i> -tolylguanidine	Deep purple
<i>o</i> -Tolylbiguanide	Vermillion
(5) Thiazoles	
Mercaptobenzothiazole	Greenish blue
Dibenzothiazole sulfide	Nil
(6) Thiourams	
Tetramethylthiouram monosulfide	Nil
Tetramethylthiouram disulfide	Nil
(7) Salts of dithioacids	
Dimethylamine dimethyldithiocarbamate	Yellowish green (slightly dirty)
Diethylamine diethyldithiocarbamate	Yellowish green (slightly dirty)
Zinc dimethyldithiocarbamate	Yellowish green
Zinc diethyldithiocarbamate	Yellowish green
Zinc ethylphenyldithiocarbamate	Yellowish green (slightly dirty)
Zinc methylphenyldithiocarbamate	Yellowish green (slightly dirty)
Piperidine pentamethylenedithiocarbamate	Dark green
Cyclohexylamine dithiocarbamate	Slightly reddish yellow
Zinc dithiocarbamate	Yellowish green
Zinc butylxanthate	Yellowish green
Sodium diethyldithiocarbamate	Yellowish green (slightly dirty)
Sodium dimethyldithiocarbamate	Yellowish green (slightly dirty)
Zinc pentamethylenedithiocarbamate	Yellowish green
Dinitrophenyl dimethyldithiocarbamate	Nil

and mercaptobenzothiazole, respectively, both of which can be easily identified by the color reaction with cobalt oleate.

(3) *Tetramethylthiouram Monosulfide and Dinitrophenyl Dimethyldithiocarbamate*.—These accelerators are easily distinguished from other accelerators by their characteristic yellow colors.

Systematic Identification of Organic Accelerators

A systematic method of identifying general organic accelerators is the following. It must be pointed out here that in every case of identification the melting point determination should always be employed as a confirmatory test.

About 0.05 g. of the purified sample to be tested is dissolved in 10 cc. of benzene (or benzene-alcohol) in a test tube and to this a few drops of a 1 per cent solution of cobalt oleate in benzene are added, the color reaction being carefully examined. Generally speaking, a purple, a yellowish green, a greenish blue or a grayish violet coloration indicates the presence of guanidines (except *o*-tolylbiguanidine), salts of dithioacids, mercaptobenzothiazole or hexamethylenetetramine, respectively. In order to identify individual members of the group, the melting point determination must be relied upon.

If the sample gives negative results for the color reaction, then it is dissolved in benzene as before, oxidized with a small amount of iodine (care must be taken not to add too much iodine), and a few drops of cobalt oleate reagent added. A characteristic greenish blue coloration indicates that the original sample is one of the thiourea accelerators.

When the sample is proved not to be a thiourea, it is dissolved in benzene again, reduced by the addition of zinc dust and dilute hydrochloric acid, and a few drops of cobalt oleate solution are introduced as before. A greenish blue or a yellowish green coloration indicates dibenzothiazole disulfide or tetramethylthiouram disulfide, respectively.

Special accelerators such as acetaldehyde-ammonia, methylenaniline, and methylene-*p*-toluidine do not give a coloration with cobalt oleate by any means, but these can be easily detected by well established methods.

Finally it must be remarked that the above method of identifying organic accelerators proposed by the author does not apply to the detection of highly colored aldehyde-amines accelerators, but these accelerators will be recognized by their characteristic odor and appearance, and so the author did not deal with them here.

Studies on the Nature of the Action of Organic Accelerators for Vulcanization

VI. Detection and Analysis of Organic Accelerators.

3. The Analysis of Water-Soluble Ultra-Accelerators and a New Colorimetric Method for the Micro-Analysis of Copper and Manganese

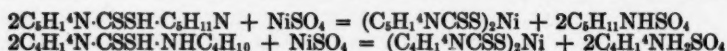
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(1) A reliable method has been described for the quantitative analysis of the so-called water-soluble dithiocarbamate accelerators, such as piperidine pentamethylenedithiocarbamate, diethylamine diethyldithiocarbamate, dimethylamine dimethyldithiocarbamate, sodium diethyldithiocarbamate and sodium dimethyldithiocarbamate. It depends upon the fact that these ultra-accelerators readily react with soluble nickel salts in solution, forming very sparingly soluble precipitates which can be estimated quantitatively by gravimetric analysis, the weight of the insoluble nickel derivatives obtained being a direct measure of the dithiocarbamate present.

Copper, cobalt and zinc react similarly with the accelerators and form sparingly soluble precipitates, respectively, but the solubilities of these metallic derivatives, determined from the results of the conductivity measurements, are about three times as large as that of the nickel derivatives; hence the precipitation of the accelerators with these metals does not give a means of evaluation by practically quantitative yields with the accelerators met with commercially.

The method of precipitation which has been worked out and ascertained to be more rapid and precise than the method described by Callan and Strafford (*J. Soc. Chem. Ind.*, 43, 7T (1924)) is as follows: 0.2 to 0.3 g. of accelerator is weighed out accurately into a 100 cc. beaker and dissolved with 50 cc. of water, any insoluble matter being filtered off and washed with a little water. The filtrate and washings are combined and suitable amounts of *N*-nickel sulfate solution added with stirring. The mixture is allowed to stand for at least 10 minutes, with occasional stirring, and is then filtered through a tared Gooch crucible and washed with cold water until the soluble sulfate is completely washed out of the precipitate. After draining at the pump, the crucible and contents are dried at 100° C., until constant in weight.



The following results were obtained with piperidine pentamethylenedithiocarbamate and diethylamine diethyldithiocarbamate.

(2) A sensitive and accurate method has been proposed for the microanalysis of copper and manganese, which is based on the fact that solutions of copper or manganese salts, when treated with aqueous solution of piperidine pentamethylenedithiocarbamate, give a brown or a brownish purple precipitate, of the composition $(C_4H_9NCSS)_2Cu$ or $(C_4H_9NCSS)_2Mn$, respectively. Experiments, show that as

small as 0.1 part of copper or manganese per million parts of distilled water can be detected colorimetrically by this method, the colors given with the new reagent being easily matched against the colors given by known copper or manganese standards. It was found, also, that the gradation in depth of color with increasing amounts of copper or manganese is excellent. The following procedure has been found to be generally applicable.

The solution containing copper or manganese, freed from other metals, is made

TABLE I
(1) *Piperidine pentamethylenedithiocarbamate*

Wt. Taken, G.	Nickel Derivative Obtained, G.	Strength, G.
0.1083	0.0832	99.74
0.2081	0.1599	99.75
0.1971	0.1515	99.74
0.1644	0.1264	99.76
0.2068	0.1589	99.75

(2) *Diethylamine diethyldithiocarbamate*

0.1774	0.1412	99.65
0.1038	0.0827	99.75
0.2092	0.1667	99.76
0.0883	0.0703	99.72
0.1768	0.1408	99.72

up to a suitable volume in a measuring flask, and an aliquot portion is pipetted into a 100 cc. cylinder, diluted with water, 10 cc. of 0.1 to 0.5% solution of the reagent added, the whole diluted to 100 cc. and well mixed. Standard comparison solutions are prepared in the same way with suitable volumes of a copper or a manganese solution containing 0.00001 g. of copper or manganese per cc. The amount of copper in the solution to be tested should not exceed 0.0002 g. per 100 cc., as above this concentration the depth of color becomes too dark for satisfactory matching.

The above method should be of particular value and interest for the determination of copper and manganese in rubber colors and rubber-proofed fabrics.

The Determination of Free Sulfur by a Volumetric Method

Part II

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In a previous paper (*Trans. Inst. Rubber Ind.*, 7, 81 (1931)) a method was described for the determination, by reduction to hydrogen sulfide, of the free sulfur in soft vulcanized rubber. This method did not involve a preliminary separation of the free sulfur by extraction of the sample with acetone, as it was shown that the combined sulfur in vulcanized rubber was not attacked by the nascent hydrogen, and there was some evidence that other organic compounds containing sulfur, such as those formed from the rubber resins and accelerators during vulcanization, did not evolve hydrogen sulfide by this treatment. Additional work has now been conducted on the behavior, under the same conditions, of organic compounds containing sulfur which are used in rubber manufacture.

The details of the estimation, as described in the previous paper, were adopted except in the case of the experiments with brown substitute. The speed of the reduction was influenced by the reducing agents employed, and tin and a mixture of equal volumes of concentrated hydrochloric acid and glacial acetic acid gave quantitative reduction in a convenient time, 1½ hours being sufficient for finely divided samples of soft vulcanized rubber. Quantitative results were obtained with tin and hydrochloric acid or with zinc and glacial acetic acid, but a much longer time of 4 to 6 hours was required; when zinc or aluminium was used with hydrochloric acid the reaction was too violent to be controlled.

Influence of Accelerators and Antioxidants

(a) *Aldehyde-Amine Compounds.*—In the previous paper it was shown that when rubber was vulcanized without an organic accelerator or with diphenylguanidine as the accelerator, the values of the free sulfur in the vulcanized rubber obtained by the reduction method and by the older methods of oxidation of the acetone extract were in agreement. It was concluded that when the reduction method gave a lower result than that obtained by the oxidation of the acetone extract, the difference was due to the presence in the extract of organic compounds containing sulfur. The whole of the sulfur in these compounds was estimated by the complete oxidation of the extract with nitric acid and potassium chlorate, but in some cases only a part was oxidized to sulfuric acid with bromine and water. In the reduction method, only a part or none of this sulfur was reduced to hydrogen sulfide, and in those cases the reduction method gave a result nearer to the true free sulfur content of the rubber. Previously it was shown that with an aldehyde-amine accelerator such as Vulcafor resin, the reduction method gave the lowest result, and the oxidation of the acetone extract with bromine and water gave a lower result than the complete oxidation method using nitric acid and potassium chlorate. A similar variation in the results given by the three methods was found with vulcanized rubber containing diphenylguanidine and "Nonox," an aldehyde-amine antioxidant. The following are typical results of a double set of estimations on a sample vulcanizate.

Composition of Sample, Parts by Weight	Free Sulfur by Reduction with Tin and Acid, %	Free Sulfur by Oxidation of the Acetone Extract	
		(1) With Bromine and Water, %	(2) With Nitric Acid and Potassium Chlorate, %
Rubber 100	1.53 1.55	1.74 1.75	1.83 1.85
Zinc oxide 5			
Sulfur 3			
Diphenyl- guanidine 1			
Nonox 1			

(b) *Thiouram Disulfide Compounds.*—A sample of rubber which had been vulcanized with tetramethylthiouram disulfide without the addition of sulfur gave a low value of 0.08 per cent free sulfur by the reduction method, but a much higher value of 0.53 per cent by the nitric acid-potassium chlorate oxidation of the acetone extract. In this case it was considered that the amount of sulfur present in the elementary state was not more than 0.08 per cent, as this rubber did not give a sulfide stain when placed in contact with polished silver, whereas another sample of rubber containing 0.20 per cent free sulfur gave a very marked stain. The following values are given as an illustration of the results obtained.

Composition of Sample, Parts by Weight	Free Sulfur by Reduction with Tin and Acid, %	Free Sulfur by Oxidation of the Acetone Extract with Nitric Acid and Potassium Chlorate, %	
		(1) With Bromine and Water, %	(2) With Nitric Acid and Potassium Chlorate, %
Rubber 100	0.06 0.08	0.52 0.54	
Whiting 45			
Carbon black 20			
Zinc oxide 10			
Stearic acid 1.5			
Tetramethylthiouram disulfide 3.5			

The accelerator, tetraethylthiouram disulfide, when boiled with tin and a mixture of glacial acetic acid and hydrochloric acid, evolved nearly 10 per cent of hydrogen sulfide, showing that a part of the sulfur in the compound was not stable toward the reducing agents. It follows that if the sample of rubber contained any unchanged thiouram disulfide, the result obtained by the reduction method although less than that obtained by the oxidation method, would be greater than the amount of elementary sulfur present.

Free Sulfur in Reclaim

A sample of tire reclaim gave a slightly lower result by the reduction method than by the nitric acid-potassium chlorate oxidation method. This sample of reclaim had 9.73 per cent acetone extract and the low result for the free sulfur obtained by the oxidation of the extract with bromine and water may have been due to occlusion of sulfur compounds in the oils and resins present. Consistent results were obtained by the reduction method, as will be seen from the following results.

TIRE RECLAIM

Free Sulfur by Reduction with Tin and Acid, %	Free Sulfur by Oxidation of the Acetone Extract	
	With Bromine and Water, %	With Nitric Acid and Potassium Chlorate, %
0.25	0.11	0.31
0.25	0.11	0.29
0.25		

Rubber Substitutes

(a) *Brown Substitute*.—Experiments were made on the application of the reduction method to the determination of the free sulfur in white and brown substitutes and in rubber mixes in which they were incorporated. Considerable difficulty was experienced, in the case of brown substitute, in obtaining consistent results both by the reduction method and by the oxidation of the acetone extract. In the case of the reduction method, the difficulty was due to the material being converted finally to a pale oil, which at the intermediate stage, being viscous presented little surface to the nascent hydrogen and the reaction was retarded considerably. A number of attempts were made to overcome this difficulty by grinding the material with inert substances such as glass wool, kieselguhr, and china clay to increase the surface, but these methods were unsuccessful as during the reaction these materials did not remain suspended in the brown substitute, but settled to the bottom of the reaction flask. The effect of the addition of different solvents, including benzene, pyridine, and *o*-dichlorobenzene, to the reducing agents was studied. Though the brown substitute was insoluble in these solvents at the initial stage of the reaction, it was converted by reduction to a material soluble in organic solvents. Solvents similar to benzene, of low specific gravity and having a low boiling point, were found unsuitable, as they floated on the top of the acid and during the reduction distilled into the absorption flask. The method which proved successful, consisted in adding 10 cc. of *o*-dichlorobenzene to the reaction mixture described in the previous paper (*loc. cit.*, p. 82) and increasing the time of heating to 2 to 2½ hours. The *o*-dichlorobenzene, having a greater specific gravity than the acid mixture, remained at the bottom of the flask in contact with the granulated tin.

The two methods used for the oxidation of the acetone extract of rubber did not give consistent results with the extract of brown substitute. The extract was not completely destroyed by the oxidizing agents, and the viscous oily residue which remained sometimes contained small amounts of sulfur compounds. The amount of sulfur and sulfur compounds soluble in acetone was determined as the difference between the total sulfur and the sulfur insoluble in acetone. These estimations were carried out by the method due to Tuttle for the total sulfur in vulcanized rubber, and by this method the organic material was destroyed by ignition. One gram of the material was placed in a 100-cc. crucible and 2 grams of potassium nitrate and 40 cc. concentrated nitric acid saturated with bromine were added. The mixture was evaporated to dryness on the water bath, 4 grams of sodium carbonate were added and the mixture stirred into a paste with the addition of a few drops of water. The contents of the crucible were then dried and gently heated to burn off the organic matter. The residue was then extracted with water, the solution was filtered, acidified with hydrochloric acid, and the sulfate formed was precipitated with barium chloride. Typical results obtained with one sample of brown substitute are given.

Total Sulfur, %	Sulfur by Reduction of Sample, %	Sulfur Insoluble in Acetone		Sulfur Soluble in Acetone	
		By Reduction, %	By Oxidation, %	By Reduction, %	By Oxidation, %
17.74	6.57	4.25	13.38	2.38	4.36
17.89	6.60	4.31	13.53	2.38	
	6.62				
	6.61				

In the case of this sample of brown substitute, 4.3 per cent sulfur was evolved as hydrogen sulfide from material which had been previously extracted with acetone and 2.4 per cent sulfur was evolved on reduction of the acetone extract. The

amounts of sulfur found by reduction of the material insoluble in acetone and of the acetone extract were less than the corresponding amounts found by oxidation. Hence sulfur compounds which were not reduced by nascent hydrogen were present in both the acetone extract and the material insoluble in acetone. As a visual examination of the acetone extract showed very few sulfur particles, it was considered that the true free sulfur content was less than the value of 2.4 per cent obtained by the reduction of the extract.

A rubber mixing was made containing 30 parts of the same sample of brown substitute as was used in the above experiments and vulcanized in a daylight press at 143° C. for 1 hour. The vulcanized material, after extraction with acetone and removal of the mineral sulfides, gave off hydrogen sulfide on reduction, but the amount was less than that given off by a corresponding amount of brown substitute in the previous experiments. The percentage of acetone-soluble sulfur, determined as the difference in the results given by the reduction of the sample and of the sample after acetone extraction, was in agreement with the amount of sulfur found by the oxidation of the acetone extract. As an example the results obtained with one sample of this mixing are given.

Composition of Sample, Parts by Weight	Sulfur by Reduction of Sample, %	Sulfur Insoluble in Acetone by Reduction, %	Sulfur Soluble in Acetone by Oxidation	
			With Bromine and Water, %	With Nitric Acid and Potassium Chlorate, %
Rubber 100				
Brown				
substitute 30	1.63	0.48	1.12	1.14
Zinc oxide 10	1.63	0.48	1.15	
Sulfur 4				
Diphenyl- guanidine 1				

During vulcanization of this mixing, 0.75 per cent sulfur was converted into mineral sulfide by reaction with the zinc oxide, and this was higher than the amounts usually formed with mixings containing similar amounts of zinc oxide, but without brown substitute.

(b) *White Substitute*.—The reduction method gave a result for the free sulfur in white substitute slightly lower than that obtained by the oxidation of the acetone extract. A typical set of results are given for a sample of white substitute of the grade manufactured for eraser mixings and containing 7.31 per cent total sulfur and 8.67 per cent total chlorine.

Free Sulfur by Reduction, %	Free Sulfur by Oxidation of the Acetone Extract With Nitric Acid and Potassium Chlorate, %
0.24	0.35
0.24	0.35
0.22	

These results showed that white substitute differed from brown substitute in the stability of the combined sulfur toward the reducing agents. The appearance of the white substitute was not changed by this treatment, whereas brown substitute under similar conditions was converted to a liquid.

In view of the results obtained with brown substitute, it was necessary to determine whether compounds evolving hydrogen sulfide on reduction were formed dur-

ing vulcanization of a rubber mixing containing white substitute. The following mixing was chosen, containing a large amount of white substitute and a high ratio of sulfur to rubber.

Composition of Sample, Parts by Weight		Sulfur Evolved on Reduction of Acetone-Insoluble Portion, %
Rubber	100	0.43 0.40
White substitute	300	
Pumice	50	
Lithopone	100	
Sulfur	30	

The vulcanized material, after acetone extraction and removal of the mineral sulfides, evolved 0.4 per cent sulfur as hydrogen sulfide on reduction. This result suggested that for vulcanized rubber containing white substitute in the amounts normally used in rubber compounding, the error from this source in the determination of the free sulfur by the reduction method will be negligible.

Free Sulfur in Hard Rubber.—The reduction method was compared with the older methods for the determination of the free sulfur in ebonite. Two samples of ebonite dust were analyzed, and it was found that the reduction method gave much higher results than the usual methods. It was also found that hydrogen sulfide was evolved on reduction of ebonite dust which had previously been extracted with acetone and also boiled with hydrochloric acid to remove mineral sulfides. Duplicate estimations gave consistent results, showing that only a definite small

Sample	Sulfur Evolved by Reduction of Sample, %	Sulfur Soluble in Acetone Evolved by Reduction, %	Sulfur Soluble in Acetone by Oxidation with Nitric Acid and Potassium Chlorate, %
Ebonite dust (containing 2% mineral matter)	9.04		5.09
Ebonite dust (containing 27% mineral matter)	3.70 3.56		1.79
Rubber 100			
Sulfur 40			
Zinc oxide 5			
Vulcafor VI accelerator 1			
(a) Vulcanized 50 min. at 121° C. in press		0.41	17.0
(b) Vulcanized 5 hours at 121° C. in press		1.12 1.05	5.10
(c) Vulcanized as for (b) and further 5 hours at 121° C. in open steam		0.58 0.58	2.77
(d) Vulcanized as for (c) and further 45 min. at 150° C. in open steam		0.72 0.79	0.94 0.85
Rubber 100		0.67 0.65 (Equivalent to 1.30% of non-loaded material)	0.09 0.11
China clay 125			
Magnesia 17			
Zinc oxide 8			
Sulfur 38			
Stearic acid 1.5			
Aldehyde-amine accelerator 2			
Vulcanized 2½ hours at 150° C. in open steam			

portion of the combined sulfur was reduced in this way. It was considered that this sulfur was not combined with the rubber by the usual addition reaction, but by another reaction, probably involving substitution. In the vulcanization of ebonite, if the temperature is allowed to become too high, another reaction takes place, evolving hydrogen sulfide and causing porosity in the vulcanized material. The methods used for preventing this second reaction consist either in reducing the temperature of vulcanization or in loading the mixture with ebonite dust or mineral fillers. Experiments showed that these methods also reduced the amount of hydrogen sulfide obtained by the reduction of ebonite previously extracted with acetone. In making the determinations, the material in the form of dust was extracted with acetone for 25 to 30 hours and then boiled with concentrated hydrochloric acid for three hours to decompose mineral sulfides.

In one sample tested, the sulfur content of the mixing was kept low, an ultra-accelerator was used and the material was vulcanized in three stages, the temperature being kept low in the first two stages. In the case of the heavily loaded material, for comparison with the other samples, the results are calculated to the basis of a non-loaded material. Some of the results obtained are given in table on page 516.

Summary

1. The method previously described for the volumetric determination of free sulfur in vulcanized rubber has been compared with the older gravimetric methods in cases where other organic compounds containing sulfur are present in the vulcanizate.

2. The volumetric method gave lower results than the methods involving oxidation of the acetone extract in the case of vulcanized rubber containing aldehyde-amine condensation products of thiouram disulfide compounds. This indicated that the sulfur combined with some organic compounds was not reduced by the reagents used.

3. The results with the accelerator tetraethylthiouram disulfide showed that in some cases part of the sulfur in organic compounds was reduced under the conditions of the reaction.

4. The acetone-soluble and the acetone-insoluble portions of brown substitute contain organic sulfur compounds. Part of the sulfur in these compounds was reduced to hydrogen sulfide by the action of nascent hydrogen.

5. The sulfur compounds present in white substitute were stable toward the reducing agents used in the estimation of free sulfur.

6. The sulfur compounds formed by the vulcanization of ebonite were in part reduced to hydrogen sulfide with tin and acid. Variations in the composition of the mixing and in the vulcanizing conditions altered the amount of these reducible compounds.

7. The volumetric method previously described cannot be used for the determination of the free sulfur in ebonite, brown substitute or in vulcanized rubber containing brown substitute. In the case of vulcanized rubber containing brown substitute or of ebonite the method can be used to determine the amount of sulfur in the acetone extract.

8. The volumetric method can be employed for the determination of the free sulfur in soft vulcanized rubber containing white substitute and in reclaimed rubber.

The author desires to thank T. J. Drakeley for his interest and help in the work.

The Volumetric Determination of Free Sulfur in Rubber

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The determination of free sulfur is probably the analytical process most frequently carried out in the chemical laboratory of a rubber factory, and it would be even more often used, could it be more quickly performed.

For the oxidation of the sulfur contained in the acetone extract from rubber, Mackay (*J. Soc. Chem. Ind.*, **49**, 401-3T (1930)) has described a rapid method which has been used in these laboratories for several years with complete success, but the sulfate produced has to be determined gravimetrically and the process is still too slow for use in factory control work. The acetone extraction of the rubber samples can usually be carried out at night on a bath with automatic time control, and if a rapid method for the determination of sulfur in the extract were available, the results of the analysis could be ready early next day. From a review of the literature the volumetric determination of sulfate by rhodizonate (Strebinger and von Zombory, *Z. anal. Chem.*, **79**, 1 (1929)) appeared to be promising, and on trial has given satisfactory results.

Method

Approximately 1 gram of the finely divided sample is extracted with boiling acetone for 6 hours. The acetone solution is transferred to a 300-cc. Kjeldahl flask of Jena glass and the solvent removed by distillation. The extract is dried at 90° and covered with 10 cc. of fuming nitric acid (d. 1.50), 5 cc. of perchloric acid (d. 1.54), and 0.5 cc. of bromine. For routine work, the nitric and perchloric acids are very easily handled in automatic measuring apparatus. The flask and its contents are then warmed gently for 30 minutes and finally boiled for 15 minutes to complete the dissolution of the extract; no "frothing" occurs when the oxidation is ended, as in the determination of total sulfur, but 15 minutes' boiling is sufficient to assure completion of the action.

The contents of the flask and rinsings are transferred to a basin and evaporated to dryness with approximately 1 gram of sodium chloride. The residue is drenched with concentrated hydrochloric acid, again evaporated to dryness, and baked for a few minutes, after which it is taken up with 200 cc. of water and 1 cc. of *N* hydrochloric acid and heated to boiling. Twenty-five cc. of standard 0.02 *N* barium chloride solution are gradually added from an automatic pipette, a drop of the liquid being tested, to ensure that there is an excess of barium chloride, by spotting on a prepared sodium rhodizonate paper. The latter is prepared by adding a drop of sodium rhodizonate solution (0.01 g. of sodium rhodizonate in 5 cc. of water) to a filter paper moistened with water, and placing the paper for about half a minute over the mouth of a flask containing a little concentrated ammonia solution (1 cc. of 0.88 d. ammonia in 1 cc. of water). A solution of sodium rhodizonate is not very stable, and is best made up every day. An excess of barium ion is indicated by a red stain.

The liquid containing an excess of barium chloride is titrated with standard 0.02 *N* sodium sulfate and when near the end point is boiled for two minutes. In

calculating the results it is usually necessary to make a deduction for sulfur present in the reagents, and the solutions are most easily standardized by determining gravimetrically the sulfate present in the sodium sulfate solution.

The following are typical results obtained.

Sample	Free Sulfur Volumetrically, %	Gravimetrically, %
1	0.25	0.26
2	0.52	0.52
3	0.48	0.43
4	0.07	0.05
5	0.21	0.17
6	0.41	0.46

The authors wish to thank the management of the North British Rubber Co., Ltd., for their permission to publish this work, which was carried out in their laboratories.

The Influence of Time on the Elongation of Soft Rubber under Constant Load

By W. W. C. Everts

LÖRRACH

According to specifications for the testing of rubber prepared by Committee Thirteen of the Deutscher Verband für die Materialprüfung der Technik, there are at the present day two common and at the same time distinct methods for studying the mechanical properties of soft rubber, *viz.*, tensile tests, and, secondly, determinations of elasticity. As carried out in practice, the tensile test is based fundamentally on the tensile testing of metals. With its great elastic properties, however, soft rubber exhibits to a very high degree changes in its elongation with time, and earlier testing methods give relatively unsatisfactory information about the effect of time during the stretching of rubber.

Of course the determination of elasticity in the specifications mentioned above, where the so-called permanent elongation is measured, gives a certain insight into this influence of time. Nevertheless this earlier method is not suitable for obtaining comparable results in all cases.

In a more extensive work, the author¹ has studied the influence of time on the elongation of different kinds of soft rubber, and has found the following empirical law applicable to the elongation:

$$\epsilon(\sigma, t) = \alpha(\sigma, t_0) + \beta(\sigma) \log \frac{t}{t_0}, \text{ where } t_0 < t < t_1 \quad (1)$$

In this formula:

- $\epsilon(\sigma, t)$ = the specific elongation as a function of the load and the time of elongation.
- σ = the specific load at the time.
- t = the time of elongation (in min.).
- t_0 = the time at which the experiment commenced (first reading of the change in elongation with time).
- t_1 = the period of time during which this formula is valid.
- $\alpha(\sigma, t_0)$ = a constant which depends upon the load and upon the time at the beginning of the experiment. When $t = t_0$, $\alpha(\sigma, t_0) = \epsilon(\sigma, t_0)$. α therefore represents the original elongation.
- $\beta(\sigma)$ = another constant, also dependent upon σ .

This formula was first developed experimentally in a simpler form by Philips,² and its validity has been confirmed by the author in detailed experiments.

As is obvious, this formula representing the elongation is valid only over a definite period of time. The limit to such a definite interval of time depends upon the characteristic structure of soft rubber. It should be borne in mind that the bond between the rubber matrix and the fillers or, in the case of pure rubber containing no filler, the residual particles of accelerator and of sulfur used for vulcanization, is wholly a mechanical one, and that these small particles in the soft rubber

are surrounded by the true rubber matrix to a certain degree like a network, without there being any chemical combination whatever.

If the soft rubber is kept in a stretched condition for a long enough time, the rubber matrix separates from these individual small particles of filler, with the formation of small vacuoles in the direction of the elongation, as shown by Schipfel.³ As a result, there is on the one hand an apparent increase in volume, and on the other hand an increase in elongation which conforms in no way to any mathematical law. This formation of vacuoles depends upon the structure of the filler, and especially upon the relative fineness of the latter. The author was able to prove that this increase in elongation takes place even under the smallest specific load, though of course only after relatively long periods of time (somewhat over 2000 minutes). On the other hand, the law of elongation given above is valid up to a point near fracture, because the phenomenon just described occurs with specifically higher loads only after about 120 minutes of application of the load.

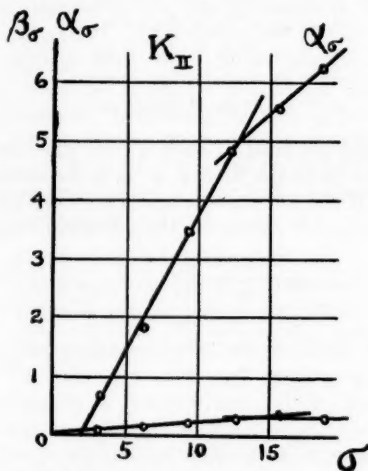


Figure 1

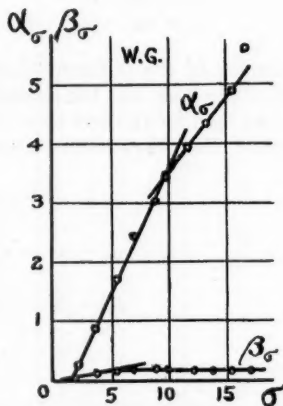


Figure 2

The series of experiments carried out by the present author, in each case with ten ring-shaped test-pieces of rubber of the same commercial kind and from the same source, shows a characteristic phenomenon in that above a definite load the constant β in the formula above is independent of σ , except for small disturbing factors which were unavoidable under the experimental conditions.

In the accompanying charts, both constants α and β are reproduced as functions of the load σ . As the diagrams show, the trend is represented in an approximate way by straight broken lines, if the part representing the smallest loads is disregarded. Since only higher specific loads and elongations are of practical interest in the case of soft rubber, there is no real objection to disregarding this range of elongation. From the tangent of the angle of slope of the straight lines, four characteristic constants can be developed. These constants can in turn be utilized to obtain a further insight into the elastic behavior of the various kinds of rubber. However, as is evident from the charts, a knowledge of four different loads is sufficient to obtain the elasticity constants, two loads previous to the break in the straight line and two loads after the break in this line. However, in order to

eliminate any possible variation resulting from differences in the quality of the samples, it is advantageous to use a greater number of different loads, *e. g.*, 6 to 10, in the investigation. As time intervals, a choice of two times for each load is sufficient.

If t_1 is the first and t_2 is the second reading of the time of elongation, then there may be derived from Formula 1 the following relations:

$$\beta = \frac{\epsilon_2 - \epsilon}{\log t_2 - \log t_1} \quad (2) \quad \begin{aligned} \alpha_1 &= \epsilon_1 - \beta \log t_1 \text{ or:} \\ \alpha_1 &= \epsilon_2 - \beta \log t_2 \end{aligned} \quad (3)$$

where ϵ_1 and ϵ_2 are the elongations at a given load for times t_1 and t_2 .

By measurements at different times, there are thus obtained for each load one value for β and two similar values for α . If now the times are so chosen that the log factor disappears, *e. g.*, $t_1 = 10$ minutes, $t_2 = 100$ minutes, then the following simple relations are obtained for the four loads necessary:

$$\begin{aligned} \epsilon_1 &= \epsilon_{12} - \epsilon_{11} & \alpha_1 &= \epsilon_{11} - \beta_1 = 2\epsilon_{11} - \epsilon_{12} \\ \epsilon_2 &= \epsilon_{22} - \epsilon_{21} & \alpha_2 &= \epsilon_{21} - \beta_2 = 2\epsilon_{21} - \epsilon_{22} \\ \epsilon_3 &= \epsilon_{32} - \epsilon_{31} & \alpha_3 &= \epsilon_{31} - \beta_3 = 2\epsilon_{31} - \epsilon_{32} \\ \epsilon_4 &= \epsilon_{42} - \epsilon_{41} & \alpha_4 &= \epsilon_{41} - \beta_4 = 2\epsilon_{41} - \epsilon_{42} \end{aligned}$$

The indices of the different elongations are read in such a way that the first index gives the load, and the second index gives the time, *e. g.*, ϵ_{31} is the elongation of the third load for the first time, etc. If the constants α and β are calculated by this method, their dependence upon the load is shown by the following relations:

$$\alpha_2 - \alpha_1 = \mu(\sigma_2 - \sigma_1) \quad \mu = \frac{\alpha_2 - \alpha_1}{\sigma_2 - \sigma_1} \quad (4)$$

$$\alpha_4 - \alpha_3 = \nu(\sigma_4 - \sigma_3) \quad \nu = \frac{\alpha_4 - \alpha_3}{\sigma_4 - \sigma_3} \quad (5)$$

$$\beta_2 - \beta_1 = \lambda(\sigma_2 - \sigma_1) \quad \lambda = \frac{\beta_2 - \beta_1}{\sigma_2 - \sigma_1} \quad (6)$$

$$\beta_k = \beta_2 = \beta_4 \quad \beta_k = \frac{\beta_2 + \beta_4}{2} \quad (7)$$

The new constants calculated from (4) to (7) are now the characteristic elasticity constants.

These constants may be expressed physically in the following way:

μ represents the slope of α below the break in the curve. The greater μ is, the faster does the elongation increase with increasing load. μ is therefore the constant of the relative "softness" (Karrer) or the constant of extensibility. Accordingly the greater μ is the more "elastic" in the practical sense is the particular rubber.

ν represents the slope of α above the break in the curve. Since with all the kinds of rubber investigated, ν was smaller than μ , a form of toughening is involved, and the relative magnitude of μ in comparison with ν can be considered as a measurement of this toughening.

λ represents the increase of β with increasing load.

β itself is a measure of the plastic part of the total elongation. The smaller β remains with increasing load, the smaller is the elongation due to the time factor. As long as β continues to increase with the load, complete recovery after release of the load is probable, though the value of β upon release may differ from the value of β under load. In so far as can be judged from various incomplete series of experiments by the author, the value of β upon release is greater than the value of β

under load. The dependence of the factor β upon σ indicates that in the samples there was still no structural change within the mass, as when $\beta = \beta_k$, i. e., when β reaches its maximum value, and no longer changes with increase in the load. The variability of β is represented by the constant λ . Therefore λ itself may be designated as the "constant of recovery." The greater is λ , the smaller is the range of loads where β is variable and where complete or nearly complete recovery after release is to be expected. Of course in this case also, the relative magnitude of the value of β may play a part.

β_k is the constant maximum value of β , which is valid for all cases where σ is greater than σ_k . Accordingly here the change in elongation with time is independent of the load, i. e., an increase in load no longer makes any difference in the change in elongation with time. Plastic flow takes place, the rate of which depends only upon the inner forces of cohesion, and it is independent of the external influence of an increase in load. β_k is the plasticity constant. The greater is β_k , the greater is the plastic range in the total elongation. Recovery after release to the original state no longer occurs, or occurs only to a partial degree, in other words there is a permanent elongation or set.

If the characteristic constants described above are grouped together under the terminology used by Karrer,⁴ the following relations are obtained:

1. μ and ν are the elastic constants.
2. λ is the pseudo-plastic constant.
3. β and β_k are the plastic constants.

The determination of these constants defines the behavior of a soft rubber upon stretching in a way which fulfills every practical need, and which also makes it possible to study the influence of vulcanization, fillers, various kinds of raw rubber and practical methods of manufacture upon the elastic behavior of soft rubber.

A few examples of these constants taken from experiments by the author are shown below:

	I	II	III	IV
μ	0.54	0.414	0.100	0.351
ν	0.20	0.247	0.0315	0.223
λ	0.0433	0.0324	0.0103	0.0217
β_k	0.173	0.156	0.0972	0.223

If the lines for α and β are idealized, as shown in Fig. 3, then there are obtained from the constants given above further factors which are of practical importance:

1. The critical load at the breaking point:

$$\sigma_k = \frac{\beta_k}{\lambda} + \sigma_0 = \sim \frac{\beta_k}{\lambda} + 1 \quad \sigma_0 \approx 1 \text{ kg. per sq. cm.} \quad (8)$$

2. The maximum elongation where recovery is possible.

$$\epsilon_r = \mu \sigma_k \quad \alpha_r = \epsilon_r \text{ when } t = 1 \text{ minute} \quad (9)$$

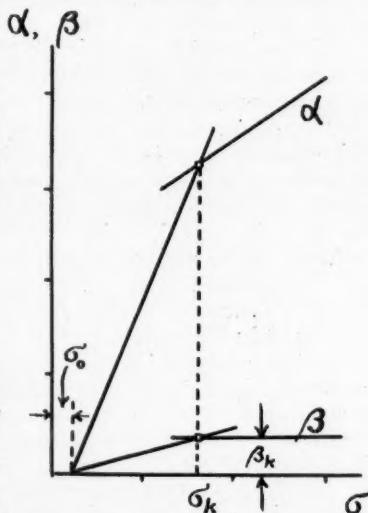


Figure 3

3. The relative danger of rupture when the critical load is exceeded, represented by the ratio $\frac{\mu}{\nu}$. The larger is $\frac{\mu}{\nu}$, the closer lies the limit of rupture to the critical load.

The relations above give by calculation the following results:

	I	II	III	IV	} kg. per sq. cm.
σ_k	5.0	5.8	10.44	11.3	
ϵ_r	2.7	2.4	1.04	3.98	
$\frac{\mu}{\gamma}$	2.65	1.67	3.17	1.57	

These values give very interesting information about the elastic behavior of different kinds of rubber. Thus, for example, the value ϵ_r indicates that rubber of type I can be stretched 370 per cent, *i. e.*, almost four times its original length, without any considerable change in plasticity. Furthermore, with the aid of these values the properties of certain kinds of rubber can be compared in great detail, *e. g.*, types I and II.

Both types have approximately the same "elasticity," and the critical load σ_k is approximately the same. Type I shows a higher value of ϵ_r , though the probability of rupture at loads where σ is greater than σ_k is essentially higher than with type II. A comparison of types III and IV is perhaps still more interesting. Both types have almost the same critical load. Type IV, however, is almost four times as elastic, and therefore the probability of rupture when σ is greater than σ_k is much less than with type III. Type III represents a so-called tough type of rubber, with relatively slight elongation and relatively greater probability of rupture at loads above the critical value of σ_k .

Type IV shows optimum values in comparison to all those given. It has a high σ_k value and a high ϵ_r value, and it can be stretched to five times its original length without any appreciable residual elongation. Finally it shows the least danger of rupture of any of the kinds of rubber investigated at loads above the critical value.

A comprehensive insight into the elastic properties of soft kinds of rubber can be obtained by the method of testing described in the present paper. Perhaps it is desirable to adopt the constants developed here as standards for characterizing the elastic properties of soft rubber in general, because they are formulated on a comparative basis and at the same time are not based on arbitrary assumptions.

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The T-50 Test for State of Cure

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In tires, machine supports, conveyor belts, hose, waterproof clothing and footwear, and other rubber articles, the state of vulcanization of the rubber in the rubber compound is important for best results in service. A simple, rapid, and accurate physical test for state of cure is described, which is independent of the composition of the rubber compound. The test depends upon the observation that for a specific rubber compound the greater the state of cure the lower is the temperature at which chilled stretched rubber will spontaneously retract.

THE state of vulcanization or cure of rubber is one of the most important characteristics of vulcanized rubber. The expressions "undercure," "proper cure," "optimum cure," "overcure," and "reversion" are indicative of the qualitative nature of ideas on state of cure. According to Whitby (?), "the term 'state of cure' is intended to indicate the position of a cure in a series of progressive cures."

The physical properties of a vulcanized rubber compound should be differentiated from the state of cure. Thus, rubber compounds suitable for tire treads, tire carcass, footwear, clothing, artificial leather, or elastic webbing are all compounded or constructed so as to bring out to the fullest extent the physical properties which are best suited to their intended use. For each of these compounds there is a state of cure which will be most satisfactory. A simple, rapid, and accurate method for measuring the state of cure would be useful, and it is the purpose of this paper to describe such a test.

HISTORICAL

Four properties have been used to determine the state of cure: combined sulfur, or free sulfur in compounds of known total sulfur; optimum cure as exemplified by maximum tensile strength, maximum stress for a given strain, or tensile product; optimum resistance to deterioration or aging; and extent of indifference to heat and cold.

It was early recognized that the amount of combined sulfur was an important criterion of state of cure. About 1843, Hancock (3) dipped raw rubber strips in molten sulfur and observed that "it was now demonstrated that sulfur and sulfur alone, blended with the rubber, and acted on by heat at a proper temperature and for a relative period of exposure to its influence, was the sole cause for the change in the substance."

As tensile-testing equipment came into use it was gradually realized that a tensile property of a single sample of rubber was of itself practically valueless in determining the state of cure, for this property depends not only on the cure but also on the quality of the rubber and the type of compound, which in turn depends upon the kind and amount of accelerator, activator of acceleration, and nonrubber additions. It became customary to make a series of cures for a given rubber compound and ascertain by tensile testing the particular vulcanizate which possessed the optimum enhancement of this property (?). This was called the "optimum cure." As artificial aging tests began to be accepted it was found that the rubber cured at this so-called "optimum" as determined by tensile tests did not always resist aging as well as rubber at some other state of cure, which was called by some the "best cure."

Goodyear (2) states in his patent that rubber when vulcanized is "so far altered in its qualities as not to become softened by the action of the solar ray or of artificial heat—nor will it be injuriously affected by exposure to cold." From the beginning it has been recognized that vulcanization conferred on rubber a tremendous change in its resistance to softening at high temperatures and hardening at low temperatures, but very little practical use has been made of this knowledge in the routine testing of rubber for state of cure.

It was observed that a well-vulcanized piece of rubber, after having been chilled in the stretched condition in contact with ice, instantly retracts on being released. Unvulcanized or undercured rubber does not snap back, but slowly returns as it is warmed. This test was so rapid and useful that for several years it was called the "ice test." Unfortunately, the range and precision of the ice test are limited; the state of cure of many compounds is beyond the range of the ice test and pieces of frozen substances which melt below the melting point of ice are not readily available. The commer-

cial production of solid carbon dioxide, however, has made it practical to evolve the present test.

THE T-50 TEST

The first step in the T-50 test consists of stretching a piece of rubber, chilling it to a low temperature while stretched, and releasing it. The rubber remains elongated, or, in other words, it is "racked." The next step consists of gradually heating the rubber and observing the temperature, T-50, at which the rubber has retracted to such an extent that it has lost 50 per cent of its original elongation. In

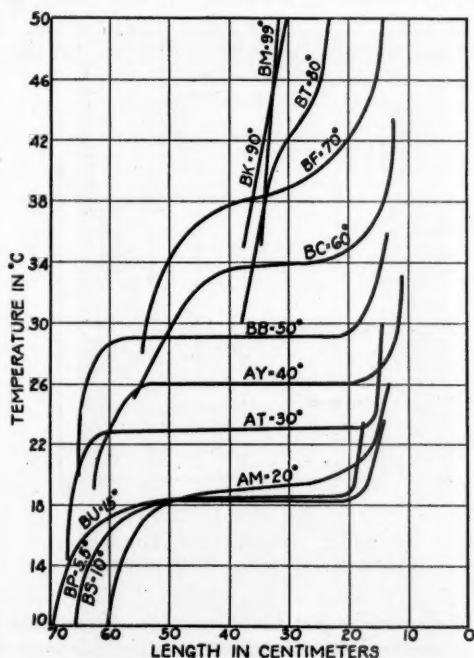


FIGURE 1. RETRACTION CURVES FOR RACKED RUBBER

many compounds, most of the retraction occurs in a fairly small temperature range, and the rate of contraction with increased temperature is usually greatest when the rubber has lost 50 per cent of its elongation.

The T-50 value for raw rubber is approximately $+18^{\circ}\text{C}$. and it decreases as the extent of cure increases. It decreases also with time of cure, and with extent of combined sulfur. The T-50 test in many cases gives good correlation with combined sulfur computed on the basis of rubber content of the compound. Roughly, every decrease of 13°C . of the T-50 value represents an increase of 1 per cent of combined

sulfur. There are sometimes large deviations from this correlation—for example, compounds containing reclaim, reverted cures, and some cases where ultra-accelerators are used, especially low-temperature cures—but this does not detract from the empirical use of the test. The test is particularly useful for these compounds after it has been standardized with a range of cures for the specific compound, since only one test piece or determination is required.

RACKED UNVULCANIZED RUBBER

When unvulcanized smoked sheet is stretched in hot water it can be drawn out to a thread. If this thread is cooled in the air and released, it remains elongated (1). In this condition the rubber is not elastic, but is more like catgut

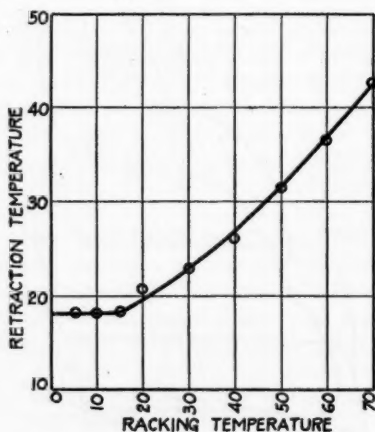


FIGURE 2. RETRACTION TEMPERATURE vs. RACKING TEMPERATURE

than rubber, and is said to be racked. When this racked rubber is warmed it retracts and again becomes elastic. This phenomenon was investigated at different temperatures of stretching. The results are of interest in that the T-50 value of raw rubber was obtained from them and also in that the relation of this T-50 value to high-temperature racking is shown.¹ Figure 1 gives heating curves of rubber which had been racked at different temperatures. The racking temperatures are shown on each curve. The rubber retracts slowly with temperature at first and then very rapidly as shown by the plateaus of the curves. Finally, on further heating, a residuum of retraction occurs. From these curves it is seen that the retraction takes place at a temperature considerably below the racking temperature, except for samples which were racked at 18° C. or lower.

¹ The authors are indebted to E. J. Joas for making these measurements.

An unexpected result is that, according to Figure 1, those racked below 20° retract at 18.2° to 18.5° C. The phenomenon has the characteristics of a melting point.

In Figure 2, the curve exhibits the relationship between retraction temperature and racking temperature. The constancy of the retraction temperature for racking temperature below 18° C. is indicative of melting phenomena. Ordinarily, the melting point of a crystal is the temperature at which the crystal is in equilibrium with the liquid. In the case of racked rubber at 18° C. the phenomenon differs from the ordinary melting point in that a state resembling

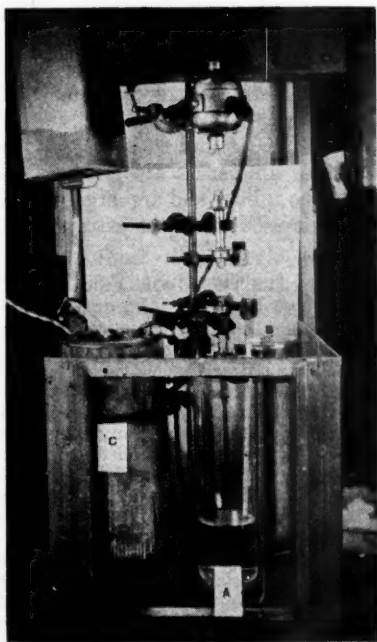


FIGURE 3. APPARATUS FOR T-50 TEST

the crystalline state produced by elongation of the rubber changes to the liquid state, which is supercooled with respect to the ordinary crystalline rubber which melts at 35° C. (6). The two changes of state are similar in that heat is absorbed as the solid is transformed to the liquid state (4, 6). Another peculiarity of the racked rubber is that the transition or retraction temperatures above 18° C. depend upon the temperature at which the racking was produced. These phenomena are, undoubtedly, correlated with the composition and structure of rubber and, eventually, should be useful in such interpretations.

T-50 VALUE OF UNVULCANIZED RUBBER

From the racking experiments, the authors have found a characteristic temperature, 18°C ., for unvulcanized rubber which is a convenient reference point for comparison with vulcanized rubber, and which has been adopted as the T-50 value for unvulcanized rubber. This retraction temperature is decreased when vulcanized rubber is tested. Obviously, since the retraction temperature of unvulcanized rubber is influenced by racking at temperatures above 18°C ., a test for state of cure above this temperature would not be satisfactory.

The T-50 value of unvulcanized rubber has been determined from the racking experiments and also by extrapolation of curve T-50 versus combined sulfur or time of cure to zero combined sulfur or time of cure. These methods agree substantially. In addition, the T-50 value of unvulcanized rubber has been determined directly for smoked sheet, latex thread, and sprayed rubber originally stretched at 700 per cent elongation, and found to be 16° , 17° , and 18°C ., respectively. These differences are probably related to the permanent set of the rubber and are largely eliminated when vulcanized rubber is used, since the extrapolated T-50 value is 18°C .

APPARATUS USED FOR T-50 TEST

TESTING DEWAR AND FITTINGS. An unsilvered Pyrex Dewar tube, called the testing Dewar, *A* (Figure 3), is mounted on a 30-inch (76-cm.) standard of 0.5-inch (1.3-cm.) iron rod. Supported in this tube are a stirrer, an electric heater, a thermometer, and a siphon tube. The stirrer is driven by a small electric motor, mounted on the standard; the speed is controlled by a variable resistance mounted in a convenient position. The current supplied to the heater is also controlled by a variable resistance. The toluene thermometer has a range of -90° to $+50^{\circ}\text{C}$.

CONDITIONING DEWAR. To the right of the testing Dewar, another Dewar tube, called the conditioning Dewar, *B*, is mounted on the standard. This contains a thermometer (-10° to $+100^{\circ}\text{C}$.) and a siphon tube.

COOLING CAN AND COIL. To the left of the testing Dewar, a double-walled copper can *C* is mounted. This contains a copper tube coil, one end of which is bent to deliver into the testing Dewar; the other end is connected by rubber tubing to a one-gallon (4-liter) can supported 1 or 2 feet (30 or 60 cm.) above it.

MOUNTING. The apparatus, except the variable resistances, is mounted on a wooden base 51×40 cm.; and is enclosed in a sheet-iron shield, with a window of Triplex glass in the front. The whole assembly can be placed on a table or bench.

RACK AND CLAMPS. The rack for

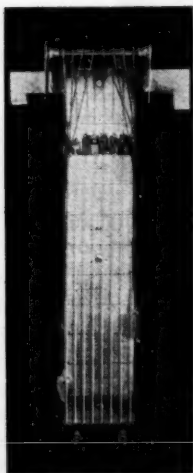


FIGURE 4. RACK FOR HOLDING SAMPLES

holding eight samples is a strip of brass about 30.6×6.38 cm. (Figure 4). A scale graduated in 0.1 inch is scratched on it. At the bottom is a clamp for holding the lower ends of the samples to be tested.

The upper clamps for died-out test pieces are individual, a separate clamp being used for each sample. Each clamp is attached to a length of silk cord, which has a glass bead strung on it, held in a fixed position by knots. The bead serves to hold the sample stretched at the desired elongation by engaging in a slot at the top of the rack. Attached to the top of the rack is a horizontal brass bar with grooves cut in it, to serve as guides to the clamp cords.

Figure 5 shows rubber test pieces in the Dewar in various stages of retraction. The long pieces are the short cures and the short pieces are the long cures. This illustrates the behavior of stock 29-92-1 for 35, 40, 45, 50, 55, 60, 65, and 70-minute cures at 141.5° C. (40 pounds steam pressure).

DIES. Special dies are used for cutting test pieces from sheets. The dies cut pieces 0.19 cm. (0.075 inch) wide, with square tabs 0.638×0.638 cm. (0.25×0.25 inch) on each end. There are three sizes of dies, giving test pieces with 2.54 cm. (1 inch), 3.82 cm. (1.5 inches), and 5.08 cm. (2 inches) length of the narrow part. This is convenient when the sample is in the form of a sheet of fairly uniform thickness, 0.051 to 0.39 cm. (0.020 to 0.15 inch) gage.

TESTING PROCEDURE

The samples of rubber are brought to a definite temperature (0° or 20° C.) in a liquid bath, stretched to a predetermined elongation, and held at that elongation while they are dipped into a bath of chilled acetone in the testing Dewar. After the temperature of -70° C. has been attained, the samples are released; they do not contract, however, but take on an almost complete set. The temperature of the bath in the testing Dewar is slowly raised; the samples contract as the temperature rises. The temperature at which the elongation of each sample is 50 per cent of the original elongation is noted as the T-50 value for the sample.

PREPARATION AND RACKING OF SAMPLES. Samples are died out with a special die. One end of each test piece is held in the clamp at the bottom of the rack, while the other end is held in an individual clamp, with silk cord attached. The cords are led through the slots at the top of the rack and down behind the rack.

FILLING THE COOLING CAN. The cooling can is filled with about 4 pounds (1.8 kg.) of pulverized solid carbon dioxide. Acetone, a little at a time, is cautiously poured into the can, stirring with a wooden rod, until the mixture forms a thick slush. More dry ice and acetone are added until the can is filled to a point about 2.5 cm. from the top, and the mixture is tamped down so that it completely surrounds the cooling coil.

The clamp is closed on the rubber tube, which connects the reservoir with the cooling coil, and about 0.5 gallon (2 liters) of acetone is put into the reservoir.

CONDITIONING THE SAMPLES. The procedure for this step differs slightly according to the stock being tested.

For unaccelerated gum stock, the conditioning Dewar is filled with ice water containing a little finely crushed ice, and the rack containing samples is placed in the Dewar and allowed to stand for 1 minute. The temperature should be 0° C. After 1

minute, the samples are stretched to the required elongation, and held there by engaging the beads on the upper clamp cords in the slots at the top of the rack. The cords are led over the guiding grooves in the bar at the top of the rack, and down outside the Dewar tube. The time when the last sample is stretched should be noted. Samples should remain stretched for 5 to 6 minutes before transferring to the testing Dewar as described below.

For accelerated gum stock, the conditioning Dewar is filled with acetone at $20^{\circ} \pm 0.2^{\circ} \text{C}$. For tread or other highly compounded stock, water at 20°C . is used.

FILLING THE TESTING DEWAR. About 3 minutes after stretching the samples, the pinchcock on the rubber tube between the reservoir and the copper coil is opened, and the testing

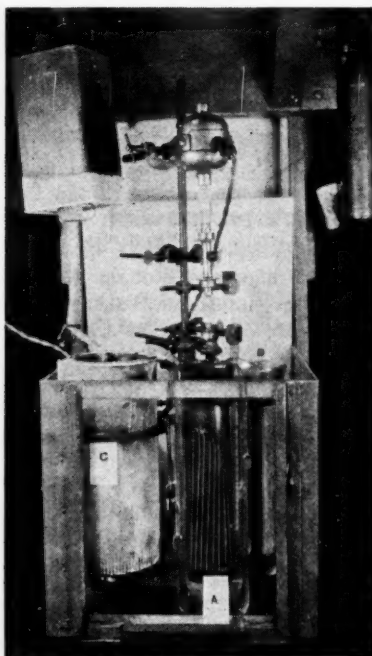


FIGURE 5. APPARATUS SHOWING TEST PIECES IN VARIOUS STAGES OF RETRACTION

Dewar is filled with cold acetone to within 1.25 cm. of the top. This takes about 1 minute.

TRANSFERRING SAMPLES. Five minutes after stretching the samples, the rack is transferred quickly to the testing Dewar, and the stirrer started and let stand about 1 minute in order to attain temperature equilibrium. The temperature of the conditioning bath is read and recorded. If the rack was immersed in a conditioning bath of ice water, this is rinsed off with acetone at a temperature below 0°C . before putting the rack in the testing Dewar.

REFILLING TESTING DEWAR. The liquid in the testing Dewar is siphoned off and poured back into the reservoir, and the testing Dewar refilled as in first filling. While refilling, the length of

each sample in the stretched condition is read and recorded as L_S . The refilling operation is repeated until the temperature falls to -70°C . or lower. Inability to reach this temperature is usually due to an insufficient supply of solid carbon dioxide in the cooling can.

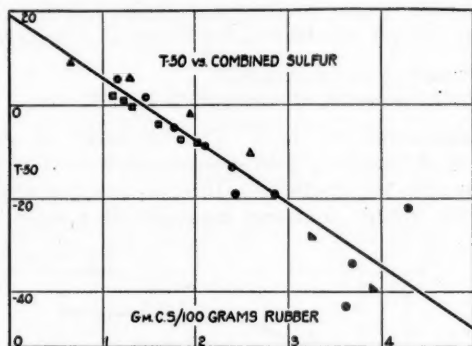


FIGURE 6. T-50 VALUES vs. COMBINED SULFUR

FREEZING TEMPERATURE. The stirrer is started, and after 1 minute the temperature is read and recorded as the freezing temperature (T_f).

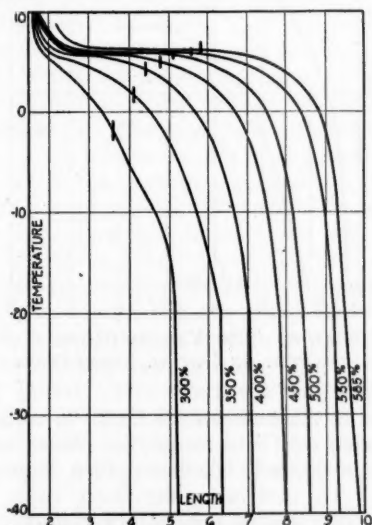


FIGURE 7. LENGTH OF RUBBER GIVEN DIFFERENT INITIAL ELONGATIONS, AS FUNCTION OF TEMPERATURE

RELEASING SAMPLES. Immediately after reaching T_f , the samples are released by pushing the beads free from notches. As quickly as possible, the length of each sample (L_f) and the temperature at which the length was read (T_1) are read and recorded. In reading the length of a sample, the sample is pulled taut, but not stretched, by means of the upper clamp cord.

CALCULATION OF L_{50} . For each sample, the length at which the elongation is 50 per cent of the original elongation is calculated, and recorded on the data sheet as L_{50} . It is easily seen that

$$L_{50} = \frac{L_1 + L_0}{2}$$

L_1 = length of stretched sample

L_0 = original length of unstretched sample

DETERMINATION OF T-50. The remainder of the test consists in determining T-50, the temperature at which the sample reaches the length L_{50} . In some cases (unaccelerated stocks) the rubber contracts gradually at a more or less

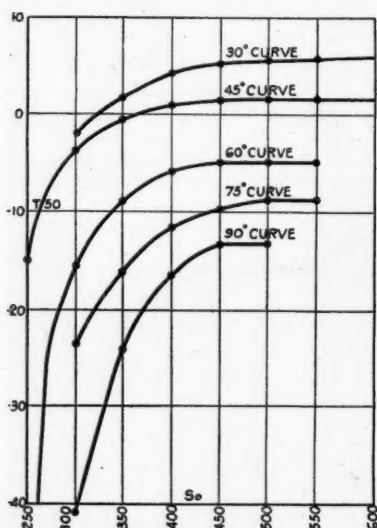


FIGURE 8. T-50 VALUES PLOTTED AS FUNCTION OF INITIAL ELONGATION

uniform rate as the temperature rises; in other cases (accelerated stocks) very little contraction occurs until a certain temperature is reached, when a sudden large contraction takes place. To determine the T-50 value accurately, especially in the case of unaccelerated stocks, the rubber must be heated slowly in the vicinity of T-50. The length of the rubber does not change when held at constant temperature, and when the temperature is increased the length becomes constant practically as soon as the test piece comes to thermal equilibrium with the bath.

The heater resistance should be adjusted to give a rise of temperature of about 5° C. per minute. After heating at this rate until within about 10° C. of T-50, the heater resistance is readjusted to slow down the rate of heating to

1° C. per minute or less. If the T-50 value is not known beforehand within 10° C., the rapid rate of heating must be discontinued before there is any danger of reaching T-50. The temperature at which the sample reaches the length L_{50} is noted, and recorded as the T-50 value. When reading the length, the sample should be held taut but not stretched.

TABLE I. CONDITIONS OF TESTING FOR DIFFERENT TYPES OF STOCKS

STOCK	CONDITIONING BATH AND TEMPERATURE	LENGTH OF TEST-PIECE		ELONGA- TION %
		Cm.	(In.)	
Unaccelerated gum	Water at 0° C.	2.54	(1)	650
Accelerated gum	Acetone at 20° C.	3.81	(1.5)	500
Tread stock and other highly compounded stocks	Water at 20° C.	5.08	(2.0)	350

EXPERIMENTAL DATA

In Figure 6 are shown the T-50 values of five different accelerated gum stocks plotted as ordinates and grams of combined sulfur per 100 grams of rubber as abscissas. A straight line was drawn through the points, showing that there is a general correlation between T-50 and combined sulfur. The chemical analyses (5) were made in the usual manner by analysis of the acetone-extracted rubber and were not corrected for sulfur combined with zinc oxide or other non-rubber constituents. The cause of the imperfect correlation is not known. This point has not been pushed to a definite conclusion, since the test was developed primarily as a measure of state of cure for a specific compound. It is satisfactory in this respect, since from a series of cures it consistently selects a given cure. The time consumed in making a T-50 run varies from 30 to 60 minutes.

In Figure 7 is shown the length of a piece of rubber, compound 29-92-I, which was given different initial elongations, L_1 , in the conditioning bath, as a function of temperature in the testing Dewar. This stock was prepared as follows: Smoked sheets, 100.0; sulfur, 3.0; zinc oxide, 5.0; hexamethylenetetramine, 1.125; and VGB (antioxidant), 1.0. It was cured 30 minutes at 141.5° C. (40 pounds steam pressure).

The T-50 values, indicated on each curve, approach a constant value as the initial elongation, L_1 , is increased, showing that it is necessary to employ sufficient elongation or the T-50 value will be too low and the extent of cure will appear too great.

In Figure 8, the T-50 values for a series of cures of compound 29-92-I are plotted as a function of initial elongation, S_0 . This plot also serves to illustrate again for different cures how the T-50 value approaches a constant value at sufficient elongation.

USES OF TEST

The T-50 test has been applied to many types of rubber compounds—smoked sheets, crepes, Para, reclaim, sprayed and latex rubber—using various fillers. The filler lithopone contains sulfur in varying amounts, making chemical analysis for combined sulfur difficult. The T-50 test simplified the estimation of state of cure, but is limited to those types of rubber which can be stretched. Thus, hard rubber, sole, tile, and heavily compounded compounds are not suitable. Carbon blacks vary in their effect on rate of cure. The test has been used to detect differences in rate of cure and to test activity of accelerators. The state of vulcanization depends upon the temperature of the rubber compound during vulcanization, and the length of time during which it is held at that temperature. In actual practice there are variables such as temperature of presses, mold lag, and differences in temperature of the top and bottom sides of the mold. The effect of these variables on state of cure can be evaluated by the test. In many laboratory tests designed to test rubber for resistance to some service condition, such as abrasion or flexing, it is much easier to interpret the results if the state of cure of the test piece is known.

The test has the advantage over tensile tests in that the width and thickness of the test piece need not be measured, but on the other hand it does not select optimum cures or the state of cure in a series of cures which will resist deterioration or abrasion. These properties must be determined independently. The utility of the test consists in the determination of the state of cure independent of physical properties which depend upon the composition.

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Presented before the Division of Rubber Chemistry at the 85th Meeting of the American Chemical Society, Washington, D. C., March 26 to 31, 1933.

Anode Process for Rubber Articles and Coatings

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THE term "anode process" has been chosen and used widely in the trade to designate a fundamental method for the production, directly from rubber latex, rapidly, and in one application, of articles and coatings of the highest grade of unmasticated rubber.

Rubber latex, a milky exudation from the bark of rubber trees, is composed chiefly of tiny particles of rubber suspended in a water phase or serum, not unlike globules of butter fat in milk. Rubber latex contains small amounts of many organic compounds and inorganic salts. Some of these non-rubber materials, such as the proteins and resins, are considered to be adsorbed on the surfaces of the rubber particles and to be responsible for many of the colloidal characteristics of latex. As it comes from the tree, the latex is unstable and coagulates easily, but, when stabilized with ammonia, it can be safely shipped and stored for long periods.

Like most colloidal particles in suspension in an alkaline medium, the rubber particles of ammoniated latex are negatively charged through the adsorption of hydroxyl anions. The particles, many as small as $1/25,000$ inch in diameter, are in constant oscillation (Brownian movement) and are kept from hitting one another and sticking together (coagulating) by the repulsion of their electric charges. When the hydroxyl ions are neutralized or otherwise removed from the particles, the electric repulsion between particles disappears and coagulation results.

Since the advent, about twelve years ago, of stable ammoniated latex as an article of commerce, intensive research and development, applied to the problem of producing a method suitable for the commercial production of rubber articles and coatings, has culminated in the development of the anode deposition process. This consists in the deposition of rubber globules and other particles suspended in an aqueous medium (compounded latex, dispersed rubber, or reclaim) upon articles and forms having the capacity

of liberating at their surfaces ions which neutralize the anionic charges of the particles.

The two principal embodiments of the anode process have been developed by the anode process pioneers at the Hungarian Rubber Goods Factory at Budapest, Hungary, and the Eastman Kodak Company of Rochester, N. Y. They may be classified as: (1) electrochemical deposition, the anode electrodeposition process; and (2) electrical-chemical deposition, the anode ionic deposition process. They are discussed in four basic U. S. patents.¹

ANODE ELECTRODEPOSITION ON METALS

A latex mix adjusted for anode electrodeposition may, for example, contain 35 per cent by weight of rubber and compounding ingredients; about 20 grams per liter of ammonia;

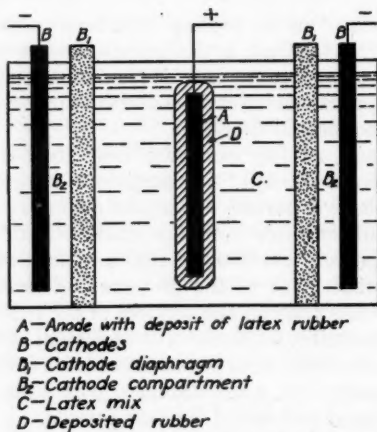


FIGURE 1. CELL FOR ANODE ELECTRO-DEPOSITION ON METAL

and about 30 grams per liter of ammonium, potassium, and sodium salts, the majority of which is ammonium chloride.

The latex mixture is placed in the anode compartment of a diaphragm cell (Figure 1). Slightly alkaline water is placed in the cathode compartment. An anode of zinc or galvanized iron is inserted into the latex, and a cathode is placed in the cathode compartment. When a unidirectional electromotive force is impressed across the electrodes, a number of phenomena take place.

Electrolysis of the dilute ammonia and ammonium chloride solutions produces at the cathode bubbles of hydrogen, and in the cathode compartment, lower hydrogen-ion concentration. It also produces at the anode electrochemical solution

¹ Sheppard and Eberlin, 1,476,374 (Dec. 4, 1923); Klein, 1,548,689 (Aug. 4, 1925); Sheppard and Beal, 1,589,325 (June 15, 1926); Klein and Szegevari, 1,825,736 (Oct. 6, 1931).

of zinc, and in the immediate neighborhood of the anode, an increased concentration of hydrogen ions and some zinc ions. The hydrogen and zinc ions which are moving away from the anode react with the hydroxyl ions adsorbed on the nearest latex particles, thus neutralizing the electric charges of those particles. The discharged particles, through their rapid Brownian movement, are immediately brought into intimate contact with one another and stick together, thus forming a compact deposit which adheres to the anode.

The negatively charged particles of rubber and compounding ingredients exhibit electrophoretic movement in the direction of the anode, bringing about a higher concentration of solids in the immediate neighborhood of that electrode.

During continued deposition the electromotive force impressed across the wet coagulated deposit on the anode removes water from it by electroendosmotic action, and compacts the deposit until it contains about 40 per cent water. This water content is sufficient to maintain the electrolytic conductivity of the deposit and permit the deposition to continue. The diaphragm which separates the latex from the water in the cathode compartment is negatively charged, and therefore the portion of the electromotive force which is impressed across the diaphragm causes an electroendosmotic flow of the positively charged water through the porous negatively charged body. Some water is also carried through the cathode diaphragm by the cations H^+ , NH^+ , Na^+ , K^+ , etc., all of which are hydrated to some extent. The water transported through the cathode diaphragm during deposition is approximately equal to the difference between the amount associated with the deposited rubber before deposition and the amount still remaining in the deposit.

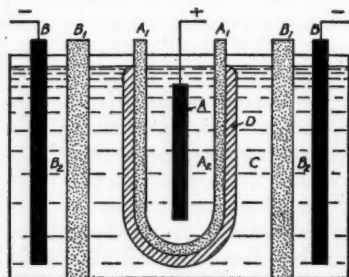
Thus, through the electrolytic production of coagulating ions and the concentration-adjusting facilities of electrophoresis and electroendosmosis, anode electrodeposition may be used for the continuous production of, for example, deposits having 60 per cent total solids from a mix containing 35 per cent total solids without depleting the mix.

ALKALINITY AND CONDUCTIVITY. For successful electrodeposition of rubber the alkalinity is controlled within fairly narrow limits whose values vary with such factors as the concentration of total solids, the conductivity, and the colloidal stability of the mix. The pH range chosen for operation under a definite set of conditions is usually that which gives firm deposits of low electrical resistance. When the pH is too low, the deposits are soft and may crack on drying; when the pH is too high, the deposits have too high electrical resistance and may overheat.

During deposition the alkalinity increases at the cathode but decreases at the anode to give essentially neutral deposits having a pH of about 6 to 7. If the cathode were immersed directly into the latex mix, the pH of the mix would increase

with continued deposition. When, however, a diaphragm is used between the cathode and the latex mix, and water is allowed to flow through the cathode compartment, the pH does not increase with deposition. In fact, in the latter case the mix slowly decreases in pH because of a slow loss of ammonia by evaporation and diffusion through the diaphragm, and ammonia must be added occasionally.

The specific conductivity is usually about 3 to 8×10^{-3} mhos per cc. The electrophoresis of the negatively charged particles is responsible for but a small portion of this conductivity, the majority being due to the ionic conduction of the bases and salts present in the mix. The base is usually ammonia, but in some cases it may be sodium hydroxide, potassium hydroxide, or amines. Chlorides or nitrates of ammo-



A—Anode
A₁—Anode diaphragm with deposit of latex rubber
A₂—Anode compartment
B—Cathode
B₁—Cathode diaphragm
B₂—Cathode compartment
C—Latex mix
D—Deposited rubber

FIGURE 2. CELL FOR ELECTRO-DEPOSITION ON POROUS FORMS

nium, potassium, or sodium are sometimes added to increase the conductivity of the latex.

When the conductivity is low, rubber deposits are likely to be very soft, but, as the conductivity is increased, the deposits become firmer and then softer again. However, moderate changes in conductivity above the minimum which is recommended for smooth, even anodic solution of the metal have much less effect upon the physical characteristics of the fresh deposits than small changes in pH. Raising the conductivity does, however, appreciably decrease the deposition factor—that is, the amount of rubber deposited per unit of quantity of electricity.

CONCENTRATION AND ELECTRICAL CHARACTERISTICS. Anode electrodeposition can be operated satisfactorily with latex mixes containing from 20 to 60 per cent total solids. Mixes of concentrations up to 35 or 40 per cent can readily be made from normal latex, but more concentrated mixes

require the use of latex from which some of the water has been removed. The concentration of mix used for a particular application depends on the price and quality of the available lattices and upon various processing details.

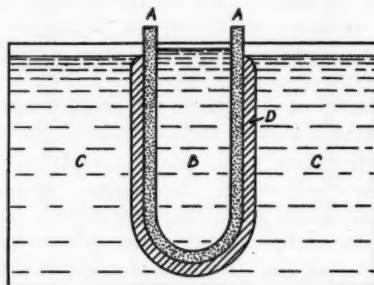
The deposition factor of latex mixes increases rapidly with concentration. For example, 35 per cent mixes of normal pH and conductivity may have deposition factors of 1.2 to 1.5 grams of dry deposit per ampere minute, but, when the concentration is increased to 55 per cent, the deposition factor is often two to four times as great. When it is considered that even 1.5 grams per ampere minute is over 24,000 grams per farad, the deposition rate of even the dilute mixes is remarkable. For example, the above figure is about 730 times the theoretical cathodic deposition rate of zinc. Taking the specific gravity of zinc as 7 and that of the rubber compound as 1, the rate of building up the thickness of deposits is 730×7 or 5110 times as fast with the rubber as with zinc. Since, however, the voltage used to deposit the rubber is usually about five to ten times that used for metal plating, the thickness of rubber obtained per kilowatt hour from a mix having a deposition factor of 1.5 grams per ampere minute is only 500 to 1000 times greater than that obtained in plating zinc.

The concentration of mixes can be maintained by electroendosmotic flow of cathode diaphragms, by replacing the deposited rubber with mixes having the same concentration as the deposits, or by removing water from the mixes by evaporation or dialysis. The use of cathode diaphragms is convenient and commercially practicable. Such diaphragms are also useful for preventing increases in alkalinity and for eliminating hydrogen frothing of the latex, which would take place if no diaphragm were used and the cathodes were immersed in the latex. When dilute mixes are used, high electroendosmotic flow is necessary to maintain the concentration, and there is considerable compacting of deposits by electrophoretic and electroendosmotic action. Sufficient electroendosmotic flow for continuous electrochemical deposition from 30 to 40 per cent mixes can readily be obtained with commercially available diaphragm material. Any variation in electroendosmotic flow which may arise after a diaphragm has been in use for some time may be compensated for by adding to the mix water or concentrated mix. When the concentration of rubber in a latex mix is increased to approach closely the concentration in the coagulated deposit, there is little need for concentration adjustment, and consequently diaphragms having little or no electroendosmotic flow are used.

When the concentration of a mix is relatively low, considerable electrophoretic movement of particles and electroendosmotic compacting of deposits takes place; but obviously, when the mix is of sufficiently high concentration, little movement of the particles is required or is even possible in the con-

tinuous building up of the deposits, and electroendosmotic compacting is limited by the decreasing permeability and increasing resistance of the deposited layer.

Thus, in anode electrodeposition, electrophoresis and electroendosmosis play valuable parts in deposition from dilute mixes, but rather unimportant roles when highly concentrated mixes are used. The "star actors" in this anode drama are the coagulating ions produced at the anode by electrolytic action and speeded on their way by an electromotive force to find negatively charged latex particles to coagulate. The velocity of the coagulating ions is the most important factor influencing the rate of deposition of rubber. In anode electrodeposition on zinc under the usual commercial conditions, the migration velocity of the zinc ions under the prevailing potential gradient largely determines the rate of formation of rubber deposits. In water at 18° C. zinc ions migrate at



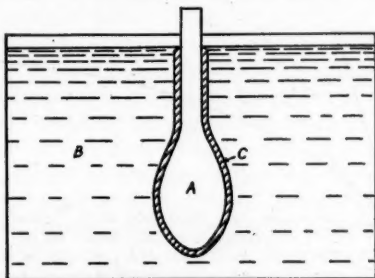
- A—Form of porous material
- B—Coagulant solution
- C—Latex mix
- D—Deposited rubber

FIGURE 3. ANODE IONIC DEPOSITION ON POROUS FORMS

approximately 0.00043 cm. per second under a potential gradient of one volt per cm., or 0.004 inch per minute with a potential gradient of one volt per inch. Thus, at the usual potential gradient of about 5 volts per inch, one might expect a deposition rate of approximately 5×0.004 inch or 0.020 inch per minute at 18° C. if the zinc ions migrated as fast through a wet coagulated deposit as in water. However, the migration of the zinc ions is considerably retarded by the continually decreasing permeability of the deposited layer. During deposition, zinc ions are precipitated as zinc hydroxide, and the concentration of zinc ions is less outside the deposit than inside. The increasing resistance of the deposit causes a greater proportion of the applied potential to be distributed across the deposit, resulting in an increase in potential gradient and temperature, both of which increase the migration velocity of the unprecipitated zinc ions. The electroendosmotic flow of water through the deposit also

has considerable influence on the migration of the ions. The final result of all these factors is an effective migration velocity of zinc ions which is considerably less than the migration velocity in water, but which is still sufficient to electrocoagulate useful deposits of latex rubber at the before-mentioned remarkably rapid rate.

A current density of 0.05 to 0.15 ampere per square inch is commonly used for the deposition of such average thicknesses of rubber as from $\frac{1}{32}$ to $\frac{1}{8}$ inch. Higher current densities, such as 0.2 to 0.6 ampere per square inch, produce smoother deposits and have better throwing power for odd-shaped articles; but such current densities cannot be used for appreciable lengths of time because of excessive heating due to the high resistance of the fresh rubber deposits. For coatings on odd-shaped articles a high current density can, however, be used to start the deposits and can later be reduced to a safe value for building up the remainder of the deposits.



*A—Form of impermeable material
with a thin coating of coagulant
B—Latex mix
C—Deposited rubber*

**FIGURE 4. ANODE IONIC DEPOSITION
ON IMPERMEABLE SURFACES**

Voltages necessary for the deposition of rubber may vary from 10 to 100 volts, depending upon the current density desired, shape of the article to be plated, size of plating vessel, the resistance of the cathode diaphragm, etc.

ANODE MATERIALS. For anode materials, metals that are readily capable of smooth, continued electrochemical solution are usually employed. Zinc is preferred for most purposes because it is one of the easiest metals to put into solution anodically in slightly alkaline solutions, because it can easily and cheaply be coated on other metals, and because its oxide, which is precipitated in finely divided form throughout the rubber, is an activator for most accelerators of vulcanization. Of the common metals, cadmium can perhaps be rated next to zinc as an anode material. It does, however, require a higher concentration of active ions for anodic solution. The color of its sulfide is objectionable for some rubber products, and its oxide is not as good an activator for vulcanization as

is zinc oxide. It is relatively easy to electrodeposit rubber upon iron and soft steel, but the presence of the finely divided iron compounds in soft rubber is objectionable from the point of view of color, cure, and aging of the rubber. Hard rubber is, however, often electrodeposited directly on iron. Rubber can be deposited upon copper and brass, but the presence of finely divided and catalytically active copper compounds rapidly deteriorates soft rubber. Aluminum has a strong tendency to be passive when used as anode in solutions of dilute alkalies with any concentration of active ions which can be used in a latex mix. Since metallic ions differ in their coagulating effect upon negatively charged colloids, the physical characteristics of wet deposits vary with the anode material.

APPLICATIONS. Anode electrodeposition of rubber is particularly well suited for the application of coatings of soft

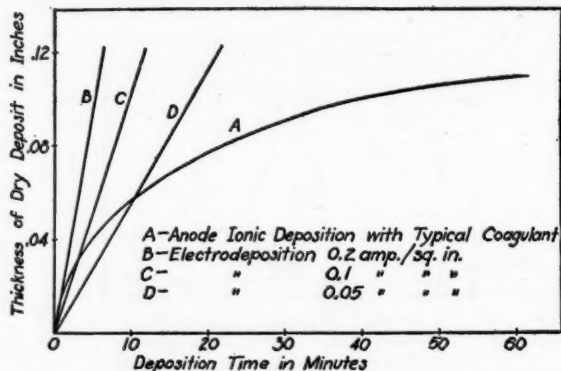


FIGURE 5. COMPARISON OF DEPOSITION RATES OF ANODE ELECTRODEPOSITION AND ANODE IONIC DEPOSITION

and hard rubber to odd-shaped metal articles. Because of the high rate of deposition a surprising volume of articles can be coated with comparatively small deposition equipment.

The process is also applicable to the production of rubber articles up to $\frac{1}{4}$ inch or more in wall thickness. The rubber is deposited on forms of zinc or of other metals coated with zinc. After several deposition cycles, the form surfaces which have become roughened by the electrochemical action are renewed by abrasion, electrolytic cleaning, or by the electrodeposition of fresh coatings of zinc.

ANODE ELECTRODEPOSITION ON PERMEABLE MATERIALS

When an anode is immersed into an electrolyte, such as a water solution of a divalent metallic salt, and this electrolyte is separated from the latex by permeable material (an anode

diaphragm), the application of a direct electric current across the cell (Figure 2) will result in the formation of a deposit of coagulated rubber upon such a diaphragm or membrane.

The mechanism of the process is as follows: Latex is concentrated in the neighborhood of the anode diaphragm surface by electrophoretic action and is coagulated by streams of positively charged cations, such as zinc, calcium, hydrogen, etc., which come through the diaphragm from the anode compartment. As in the case of electrocoagulation directly upon the metal anode, the deposit is compacted by electrophoretic action, the pH of the latex mixture is prevented from increasing by the migration of cations into the cathode compartment, and the concentration of the mix is maintained by means of electroendosmotic transfer of water through the cathode diaphragm into the cathode compartment.

When this process is used to produce rubber articles, the forms are made of a material having the greatest possible porosity consistent with a dense homogeneous surface and sufficient strength. Certain varieties of ceramic materials satisfactorily meet these conditions. Such forms can be provided with raised or depressed designs, negatives of which are accurately produced on the rubber articles. The designs on the forms are permanent, and are not eaten away by electrochemical action as are fine designs on zinc anode forms. After a certain number of depositions, however, the resistance of the porous material rises because of polarization effects; but this condition can be remedied by immersing the diaphragms in an electrolyte and passing a direct current through them for a short time in the direction opposite to that used in deposition.

This process has also been used for the application of permanent coatings to materials whose pores are fine enough to prevent the passage of the latex particles and to materials of coarser porosity which can be rendered temporarily microporous by the application of colloids or other materials. Colloids used for this purpose sometimes contain coagulating ions which diffuse into the latex sufficiently to form a thin microporous layer of coagulated rubber which acts as a diaphragm for further coagulation by ions migrating under an impressed electric potential. Such a process may be considered a combination of electrodeposition with ionic deposition.

ANODE IONIC DEPOSITION

In anode electrodeposition from concentrated mixes, electrophoretic and electroendosmotic action are incidental to, rather than vital to, the coagulation of deposits. In such deposition the applied electric potential fulfils the primary function of causing coagulating ions to migrate from an anode surface or from the anode compartment of a diaphragm cell to coagulate negatively charged particles into useful deposits.

of latex rubber. It is clearly obvious that, if coagulating ions were allowed to diffuse from surfaces or through permeable materials into a concentrated latex mix, the same result would be accomplished, but at a considerably different rate. Accordingly, there has been developed simultaneously with electrodeposition, or (to use a more descriptive term) electrochemical deposition, a process in which the coagulating ions are provided directly by chemicals and without electrochemical action, and in which the streams of coagulating ions are impelled outward from the depositing surface by osmotic pressure rather than by an applied electric potential. Since this process also involves the removal of the negative electric charge of the suspended particles by positively charged ions moving from a surface into the latex, it has been termed "anode electrical-chemical" or "ionic deposition."

Equipment such as that illustrated in Figure 2 for use in electrodeposition on porous diaphragms may also be used for ionic deposition, but in such case no external source of electric current and no cathode diaphragm are required. Coagulating ions readily diffuse from the pores of permeable surfaces to coagulate deposits of latex rubber (Figure 3). When the pores extend entirely through the walls of the depositing backing, an unlimited reserve of coagulating ions can be provided to diffuse through the porous walls for continuous or multiple deposition. Coagulant can also be applied to the deposition side of a permeable form by immersing the form in a coagulant solution or by any other convenient means.

When articles or forms with impermeable surfaces are to be coated with rubber, the coagulating ions are often provided on the surfaces by dipping or otherwise coating with solutions of polyvalent metallic salts, inorganic acids, organic acids, or any other desired latex coagulants, and by allowing the excess solvent to evaporate. The forms can also be coated with coagulants by dipping in molten salts or acids or exposing to acid vapors. When such coagulant-coated surfaces are immersed in latex, the ions diffuse and coagulate deposits of latex rubber (Figure 4).

The initial rate of ion diffusion and consequent rubber deposition is very high, but, as the thickness of a deposit increases, the rate of deposition decreases in accord with the law of diffusion, as is indicated by the shape of curve *A* in Figure 5, which shows the deposition rate of a typical coagulant when applied as a thin film on an impermeable surface. For comparison, curves *B*, *C*, and *D* show deposition rates obtained by anode electrodeposition at constant current-density values in the usual commercial range. It is evident that ionic deposition compares favorably with electrodeposition in the rate of building up of deposits up to 0.030 to 0.040 inch in thickness of dry rubber. Both methods can be used to produce deposits up to 0.25 inch or more in thickness,

but in such a case the time required is much less with electrodeposition.

Anode ionic deposition is readily adaptable to the production of a wide variety of rubber articles on forms of metal, porcelain, plastics, and many other permeable or impermeable materials. It can also be used to apply permanent coatings to an even greater variety of materials in a wide range of shapes and sizes.

PROCESSING ANODE DEPOSITS

Fresh deposits of anode rubber contain 30 to 60 per cent by weight of water, which is distributed through the network of coagulated particles of rubber and compounding ingredients in a fairly continuous phase. Deposits of such structure can, of course, be readily washed if desired. Drying is carried out under temperature and humidity control, the conditions of which vary with different articles. When the deposits are dry, they are given the necessary hot cure in steam, air, or any other convenient gaseous or liquid medium. Rubber-covered articles are cured under conditions specifically designed to give the maximum possible adhesion of the rubber to the article surfaces.

COMMERCIAL APPLICATIONS

ANODE PROCESS RUBBER ARTICLES. Many relatively thin rubber articles, such as balloons and gloves, have long been made by the repeated dipping of forms into rubber cement. This method often requires several hours to build up the necessary thickness of deposits, and has other disadvantages such as fire and health hazards, limitations in compounding and curing ingredients, and inferior chemical and physical properties. Thin articles can also be made by repeated dipping in latex, but such a multiple dip method also has marked disadvantages, such as the formation of striations and layers, separation of the layers under stress, the entrapment of air, and slow rates of thickness building. For example, it would require a number of individual dips and a like number of drying intervals to produce $\frac{1}{32}$ inch in thickness. With the anode process, on the other hand, homogeneous deposits free from defects are produced in one application, and the time required for most articles is measured in seconds and minutes rather than in hours.

Anode rubber has extraordinary strength and durability. Tensile and elongation data such as 5900 pounds per square inch at 970 per cent elongation and 6700 pounds at 925 per cent are characteristic of anode compounds but are most difficult to obtain with masticated rubber. Remarkably high tear resistance is exhibited by anode rubber stocks all the way from the uncured state to the point of optimum cure. It has good resistance to wear, abrasion, and corrosive chemicals. The water absorption can be controlled to a value

comparable with that of good masticated rubber and very much less than that of gum-dipped rubber.

Rubber products that are at present being manufactured by the anode process include gloves, balloons, drug sundries, fountain pen sacs, bathing caps, rubber overshoes, and many specialties.

ARTICLES COVERED WITH ANODE PROCESS RUBBER. For many years engineers have been specifying rubber-lined tanks and other types of rubber-covered equipment for resistance to severe corrosive conditions and for other specific uses. However, the application of rubber coatings by hand (paper-hanging method) is too expensive for wide use on small odd-shaped articles. Now the anode process has ushered in a new era in which articles of countless shapes and sizes can be efficiently and inexpensively covered with adherent coatings of soft and hard rubber.

A high degree of adhesion to metal and many types of non-metal surfaces can be obtained through the use of Vulcalock (a rubber isomer of remarkable adhesive properties) which can be applied to article surfaces by anode process deposition from water dispersions or by dipping in solvent solutions.

Anode soft and hard rubber coatings are used for such varied purposes as resistance to corrosive chemicals; resistance to wear and abrasion; insulation against electricity, heat, sound, and vibration; and for specific applications.

ACKNOWLEDGMENT

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Zinc Oxide in Rubber

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THERE are few secrets in the zinc industry, as in most industries, but there has been a reticence to permit the publication of articles regarding the industry that has reacted to its detriment. There is, accordingly, comparatively little literature, and much of that part of this paper that relates to the manufacture of zinc oxide is taken from carefully selected patents. The validity of many of these is questionable, since they have never been litigated, and no claims are made regarding their value except that they

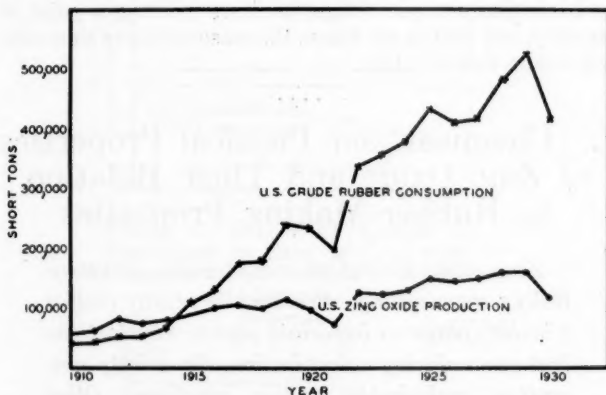


FIGURE 1. CRUDE RUBBER CONSUMPTION AND ZINC OXIDE PRODUCTION FOR U. S.

describe the processes used in the industry more satisfactorily than can be found elsewhere.

The methods of making zinc oxide can be only outlined in the space available, and it is to be hoped that additional information will be presented by those who find the discussion incomplete.

There is considerable misunderstanding among nonrubber technologists regarding the use of zinc oxide. It is hardly necessary at the present time to remind rubber technologists that zinc oxide is not a filler, inasmuch as the cost on volume basis is approximately ten times that of rubber, without con-

sidering the cost of incorporating it into rubber. It is used largely as an essential chemical ingredient and its chemistry is a matter of first importance.

The amount of rubber used in industry has increased rapidly in the past two decades (Figure 1), but the amount of zinc oxide produced has increased comparatively little. Of this zinc oxide, perhaps half or two-thirds has been used by the rubber industry and the balance by the paint industry which utilizes approximately 20 per cent additional leaded zinc oxide.

The consumption trend has continually changed, working one way for one rubber product and the reverse direction for others. Today the number of rubber products that contain zinc oxide has increased until practically all contain some; but the percentages have decreased to comparatively small amounts, although in the case of solid tires (which are gradually disappearing from the highway because of pneumatic tire competition) the percentage has increased to as much as 65 per cent by weight. Against the general trend to lower zinc contents, the tendency has been to increase the amount of zinc oxide in the carcass compounds of heavy-duty pneumatic truck tires to 30 or 40 per cent by weight. It seems probable that the percentages used are reaching a point of stability, and that in the future the consumption of zinc oxide will follow that of rubber.

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I. Chemical and Physical Properties of Zinc Oxide and Their Relation to Rubber-Making Properties

Zinc oxide for rubber compounding is essentially a chemical ingredient and the acidity (sulfur trioxide) plays an important part in the reactions that occur during vulcanization, the acidity preventing undesirable protein reactions. Other chemical ingredients to be considered are small amounts of lead, cadmium, and fatty acid. The physical properties that affect the behavior of zinc oxide in rubber are particle size, uniformity of size, and particle shape; these influence the incorporation of the zinc oxide in rubber and the reinforcement when large amounts are used.

ZINC OXIDE is manufactured by two general methods. In the first, it is made directly from ore and the process is known as the American. In the second, or French process, zinc metal is first produced and the oxide is made by volatilizing and burning the vapor in air. The outstanding

difference in the oxides made by these two methods lies in the amount of sulfur adsorbed on, or combined with, the zinc oxide; the American process oxide contains sulfur, and the French process oxide is substantially free from it.

CHEMICAL PROPERTIES

Sulfur is necessary in many industries, including rubber manufacturing, and it is an injurious impurity in other products. When present in uniform amounts in zinc oxide, it has both advantages and disadvantages. On the surface of zinc oxide particles it exists as adsorbed sulfur trioxide or chemically combined as zinc sulfate, and as a basic zinc sulfate. Since sulfur trioxide and zinc sulfate are acidic, the incorporation of this sulfated zinc oxide makes the rubber slightly

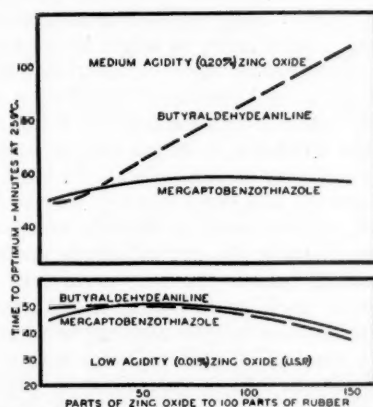


FIGURE 2. EFFECT OF ACIDITY OF ZINC OXIDE ON RATE OF CURE WITH BOTH ACID AND ALKALINE ACCELERATORS

Rubber	FORMULAS	
	100	100
Sulfur	3	3
Mercaptobenzothiazole	1	..
Butyraldehyde aniline	...	1
Stearic acid	2	...
Zinc oxide	5-150	5-150

acid, rather than slightly alkaline or neutral as in the case of a nonsulfated zinc oxide. This acidity prevents the zinc oxide from reacting with the proteins which exist in appreciable amounts in the crude rubber and thereby improves factory processing. Stocks containing American process zinc oxide mill relatively smoothly, and tube and calender with smooth surfaces and clean edges. It has been stated that plant foremen can see this improvement when American process zinc oxide has been used in a tread stock containing only 4 to 5 per cent zinc oxide. Processing is one reason that acid zinc oxide is frequently chosen for inner tube manufacture. When a stock is alkaline, zinc oxide reacts with protein in the

rubber, and a semi-rigid structure develops that makes the stock heterogeneous and harsh, and accounts for the inferior factory working properties. In no instance is homogeneity more desirable than where a stock has to be flexed; Gibbons (11, 12, 16) recommends the addition of strongly acid materials such as zinc chloride to rubber compounds with extra accelerator to overcome the retardation of cure caused by the acid. In the case of a certain compound he obtained more than double the flexing life through the addition of acid material. An acid zinc oxide will furnish enough acidity to prevent the zinc protein reaction in most stocks, and comparatively large amounts of acid zinc oxide may overcome the alkalinity caused by alkaline compounding ingredients. Acidity has been shown to improve not only the factory working and flexing of stocks but also the scorch resistance (17).

The cure of rubber stocks is faster in alkaline stocks than in acid stocks. Accordingly, as might be expected, rubber containing French process oxides tends to cure more rapidly than rubber containing American process oxides, and the difference in cure increases with the amount of zinc oxide in the compound; the difference in curing rate is negligible when only 10 to 15 per cent is used. In stocks accelerated with organic accelerators, the effect depends on the kind of accelerator used. In the case of alkaline accelerators, such as diphenylguanidine or the butyraldehyde aniline accelerators, acid material retards the cure more than it does for acid accelerators, such as mercaptobenzothiazole and the thiurams. Irrespective of the amount of zinc oxide and, therefore, the amount of acid material within limits, the time to the optimum cure is approximately the same when mercaptobenzothiazole is used; but with butyraldehyde aniline the time required to reach the optimum increases with the amount of acid zinc oxide (Figure 2).

The effect of adding more accelerator is to increase the accelerator cost, but, since accelerators often have antioxidant properties, the antioxidant cost may be correspondingly decreased. The acid effect can be largely overcome by adding alkaline materials, but in this case the advantages of the acid material are lost.

In one phase of rubber compounding, acid zinc oxide may be undesirable. Zinc sulfate is hygroscopic and tends to absorb water even when compounded in a rubber stock. Accordingly, a stock may swell too greatly to be suitable for a packing in a water pump, although the same packing may show no deleterious effects when used in nonhygroscopic solvents. Similarly, in the case of electrical insulation, the dielectric constant of water is 80 and of rubber is 2.5. The absorption of water will accordingly cause undesirably high dielectric constants, and it will also increase the electrical leakage. In commercial practice, however, where the amount of zinc oxide added is not great and where lime or litharge is

used in the compound, the injurious effect of the hygroscopic material may be largely or wholly overcome.

The addition of 10 parts of litharge to the following compound containing American process zinc oxide reduced the swelling in water of thin sheet rubber from 50 to less than 20 per cent, which is comparable with the swelling developed by thin sheets of rubber containing French process zinc oxide:

Rubber	100
Sulfur	3.25
Stearic acid	1
Zinc oxide	120
Diphenylguanidine	0.25

It is evident either that the zinc sulfate migrated to the litharge or that lead soaps migrated to the zinc sulfate. Migration of the zinc sulfate is improbable; it has been shown (7) that sulfuric acid stored in rubber-lined tanks will not leach zinc oxide compounded in the rubber.

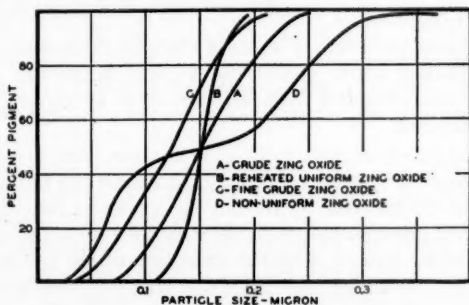


FIGURE 3. SIZE DISTRIBUTION CURVES

(There is no implication that oxide B is obtained by heating either A or C. These curves have to be estimates since no really accurate size distribution curves have been made on fine pigments.)

As another example of the reaction in rubber between litharge and zinc sulfate, an oxide with an excess of litharge that gave a gray stock was mixed with another containing an excess of sulfur trioxide, and a white stock was obtained. The sulfur trioxide in the one oxide reacted with the litharge in the other to form inert lead sulfate, and this reaction must have taken place during milling.

Zinc oxides containing excessive amounts of acid material may form pellets of unmixed pigment when incorporated in rubber. This pellet formation does not develop except in internal mixers unless the amount of acid material is much greater than is present in the oxides used in the rubber industry today. Some years ago, oxides with high water-soluble salt contents were sold to the rubber trade in the same car with oxides of low water-soluble content, and the amounts of acid were so great that unskilled workmen in the plant could separate the lots by noting the unmixed pellets that formed during milling. The amounts of acid were so large that tensile

strength determinations in a rate-of-cure formula that was used showed variations from 400 to 2800 pounds per square inch among the lots. Today the variation is rarely more than a couple of hundred pounds in the same formula, and the acid American process zinc oxide mixes at least as well as the low-acidity French process zinc oxide on the mills. When inclosed mixers are used, special procedures have been worked out by which American process zinc oxide has been satisfactorily handled in certain plants. Some technologists have gone so far as to say that the whole problem of Banbury mixing is one of mixing procedure rather than of oxide characteristics. Other technologists take the viewpoint that no zinc oxides mix satisfactorily in the internal mixer, and they prefer to add the oxide on the rolls.

In a few cases, rubber mixed with French process oxides in an inclosed mixer has pulverized and could not be made to coalesce. The same phenomenon has also been observed in mixing on the mills where stocks appear to be burned without any sulfur being present. The most reasonable explanation is that the protein in the crude rubber (high in protein and low in fatty acid) reacted with the zinc oxide to give it the burned appearance.

In addition to sulfur, zinc oxide may contain various other ingredients such as lead and cadmium, but these are as likely to be found in oxides made by the one process as by the other. As a matter of interest, one of the zinc oxides analyzing highest in zinc oxide content, with the exception of the sulfur, is an American process zinc oxide, and one that analyzes lowest is a French process zinc oxide.

Copper and chlorine, especially the former, are undesirable ingredients in zinc oxides because of their influence in causing rubber to deteriorate (age). At the present time none of the standard zinc oxides on the market has enough of either of these materials so that they need be seriously considered.

Lead exists in American process zinc oxide as lead sulfate, and in French process oxides as free lead oxide that will react with proteins to form products that cause fast cures with mercaptobenzothiazole. It is questionable whether this method of obtaining acceleration is desirable since Dinsmore (8) reports lower abrasion resistance for mercaptobenzothiazole-diphenyl guanidine accelerated stocks. Free lead oxide (13) will also retard thiuram-accelerated compounds. Lead as lead sulfate is inert except in alkaline stocks when some of the lead may go into solution and prevent a desirable white color. Thompson and Bratby (18) recommend as a matter of safety not over 0.1 per cent lead and preferably lower. It probably does little harm in black stocks. Lead obtained its bad name largely because it was associated with variable amounts of sulfur rather than with uniform amounts, and, accordingly, the rate of cure was nonuniform.

Cadmium exists in American process oxide at least partly as cadmium sulfate, which is water-soluble and retards thiuram stocks (9), but there is evidence that it enables other accelerators to cure more satisfactorily (possibly by absorbing hydrogen sulfide that tends to decompose the zinc accelerator compound); it is accordingly considered desirable by some rubber manufacturers and undesirable by others. Cadmium is also of value in retarding scorching (4) in the case of thiuram accelerators.

Some oxides have been offered to the trade, surface-treated with fatty acid that is deposited on the surface and that exists as free acid or as the zinc soap. The purpose of adding this material has been to change the surface characteristics from inorganic to organic, similar to rubber. Fatty acid is soluble in rubber, and a surface coating of this material is intended to pull the zinc oxide particle into the rubber during mixing by virtue of the solution pressure of the stearic acid molecule. The fatty acids most frequently found at present are commercial stearic consisting largely of stearic $[\text{CH}_3(\text{CH}_2)_{16}\text{COOH}]$ and palmitic $[\text{CH}_3(\text{CH}_2)_{14}\text{COOH}]$ acids, and the fatty acids from coconut oil that consists of lauric $[\text{CH}_3(\text{CH}_2)_{10}\text{COOH}]$ acid with some other acids of the same series of both higher and lower molecular weights.

Fatty acid on the surface of zinc oxide is conceded to act chemically about the same as an equivalent amount of fatty acid added to the rubber.

In general, the fatty acid treatment has failed to achieve all that had been hoped for it in the way of improved Banbury mixing and shorter mixing time. Some surface-treated zinc oxides that appear to disperse well in rubber form many small unmixed pellets that are seen when the stock is examined microscopically. In the case of certain mixing schedules, however, there are reports of faster mixing. In other cases difficulties have been reported due to fatty acid lubrication of sides of the mixer that allowed slippage and at times caused the mix to pulverize.

The use of acid surface treatment is fairly old. Zinc oxide was surface-treated in the nineteenth century (14) with fatty acid to improve its mixing qualities in oil. Without going into the large number of patents on this subject, it should be noted that the process has become commercial in the case of lithopone which is treated commercially with soaps (2) and with free fatty acids (15) to improve the mixing in paint oils.

PHYSICAL PROPERTIES

Particle size embraces not only the average particle size but the distribution of sizes (Figure 3). Two oxides could be of the same average particle size—for example, 0.2 microns—and yet 90 per cent of the particles in the one pigment might have a particle size within 20 per cent of the average,

whereas in the other case not over 40 per cent would have particle sizes within this range. There has been considerable discussion as to whether a uniform pigment or a nonuniform pigment is desirable. It would seem, however, that the weight of evidence strongly favors a uniform particle size. Fine particles (10) mix into rubber with more difficulty than the coarser ones; they develop less resilient stocks and are more likely to cause scorching. Accordingly, it would seem desirable to eliminate them. The poor mixing of fines in zinc oxide can be compared directly with the frequently noted poor mixing of sulfur and of accelerators that contain too much fine material.

It has long been thought that fine pigments activated better than coarser ones, but recent data (5) have indicated that particle size has little influence, as might have been expected

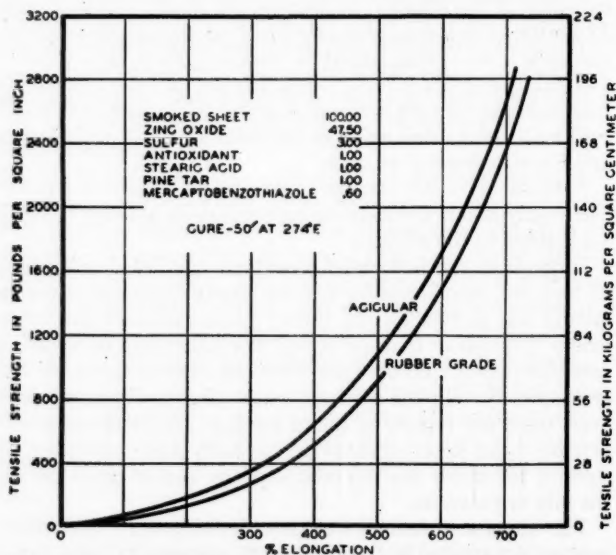


FIGURE 4. STRESS-STRAIN CURVES COMPARING ACICULAR WITH NONACICULAR ZINC OXIDES

on a theoretical basis. Activation is the reaction of zinc with the accelerator to form the zinc accelerator compound; the reactions between fatty acid present in the rubber and zinc oxide, and, in turn, between the zinc soap so formed and the accelerator, are so rapid that, irrespective of the particle size of the zinc oxide, there is sufficient time for the zinc salt of the accelerator to be formed during processing. Accordingly, it is necessary only for the zinc present to act as a reservoir to replace any zinc that has been precipitated by hydrogen sulfide during curing and to form zinc soaps which, by mass action, will keep a large percentage of the accelerator in the

form of the zinc compound. Relatively coarse zinc oxide is as capable of forming the accelerating zinc compounds as the finer zinc oxides.

Several years ago when a zinc oxide of fine particle size was offered to the trade, there was considerable speculation as to whether small amounts of this oxide could be used in the place of larger amounts of ordinary oxide, but laboratory tests and commercial experience have shown that the finer particles do not make it possible to reduce the quantity. In fact, in certain cases the fine zinc oxide actually has tested unsatisfactorily, owing to adsorption of some of the curing ingredients. It seems reasonable that the differences that have been noted in the activating properties of zinc oxides are due to differences in the kind and amount of nonzinc constituents, such as sulfur, lead, and cadmium, rather than in the physical characteristics.

When larger amounts of zinc oxide (50 per cent by weight) are used, the reinforcing properties of the oxide come into play, and the finer particles tend to develop higher tensile strengths. It is frequently necessary, however, from the factory working viewpoint to add more fatty acid in the case of the finer zinc oxides; this addition lowers the reinforcement of the compound to a point where it is little better than if coarser zinc oxides had been used.

It is obvious that, when only 5 per cent of zinc oxide is used in a carbon black stock and part of this zinc oxide goes into solution, the change of reinforcement that this one volume of zinc oxide will make in a mix containing 100 volumes of rubber and perhaps 25 volumes of carbon black will not be measurable.

In the case of American process oxides, particle size has little influence on the rate of cure, but in the case of French process oxides, the finer particle sizes accelerate the cure when large amounts are used (3). Although this paper is intended to be a summary of facts rather than theories, it may be helpful to point out that zinc polysulfides (1) are curing ingredients, and that, when large amounts of zinc surfaces are present, sufficient amounts of zinc polysulfides may be formed in alkaline stocks to account for the acceleration.

The oxides that have been discussed approximate spheres; that is, no one dimension tends to predominate. Oxides of unusual shape can be made, however. The particles in one of the photomicrographs consist almost entirely of needles. These needles apparently mill into rubber and develop a strawstack structure, and thereby stiffen the rubber as shown by the stress-strain curves in Figure 4. Acicular zinc oxide is desirable where specifications require stiffness; it is also desirable where stiffness will develop superior service life, possibly in air bags. At present this grade of oxide is used largely in paint where it reduces checking and cracking.

With reference to grit, nothing can be said in its favor. It has no virtues and serves only to lower tear resistance and to increase the possibility of flexing failure.

Optical properties are determined basically by the refractive index which is fixed as definitely as specific gravity. The actual whiteness of rubber containing different zinc oxides, however, depends on particle size, chemical properties, and cleanliness. Often the color of the compounded rubber depends on the chemical ingredients in the zinc oxide more than on the whiteness of the zinc oxide itself. However, if the zinc oxide is too dirty, caused, for example, by carbon from electrodes, it will not be possible to obtain the best whites.

The whitening strength, which refers to the ability of the pigment to overcome the dark color of the rubber-sulfur compound, depends on the particle size of the zinc oxide, and it has been shown that the optimum whitening in rubber (6) is obtained with zinc oxides of about 0.15 micron (Goodyear scale) which is about the size of most commercial zinc oxides. Referring again to the question of uniformity of particle size, an oxide containing a range of particle sizes, some extremely small and some coarse, will have a much lower whitening strength than an oxide consisting largely of uniform particles, in the neighborhood of 0.15 micron in diameter.

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II. Choice and Testing of Zinc Oxide for Rubber Compounding

The choice of a zinc oxide for rubber compounding depends on the methods of factory processing, the kind of products made, and the type of formulas that are compounded. In choosing a zinc oxide, it is desirable to use rubber tests. Present-day uniformity of shipments is high, but, if uniformity tests are desired, pigment tests, including analytical and microscopic, may be used.

THE choice of a zinc oxide for rubber compounding involves widely different problems in different plants. One company has built up its processes around the smoothness of factory processing and freedom from scorch; another, on Banbury mixing; a third, on electrical properties; and a fourth, on acceleration costs. It would be inconvenient if they were unable to obtain the kind of zinc oxide that they have found desirable; yet if there were only one zinc oxide, and if that one were any one of the standard zinc oxides that will produce white rubber products, rubber compounders state that they would be able to modify their formulas and processes so that their products would continue to be of high quality. Nevertheless, there are differences in zinc oxide and it is desirable to understand these oxides so that the compounder will be able to choose the one best suited to his needs.

In the case of some plants it is desirable to use two, three, or more different zinc oxides in order to obtain their specific advantages. But in many cases the plant is limited to one oxide, and it is necessary to choose and to adjust the compounds so that they will work with this oxide.

For example, an acid zinc oxide could be chosen for general use, and, in the few cases where large amounts are to be used with alkaline accelerators, the excess acidity would be neutralized with hydrated lime as shown in Figure 1. In this example 1.5 parts of lime neutralized the excess acidity of 100 parts of a zinc oxide having an acidity of 0.2 per cent and brought the curing curve (tensile strength vs. time) slightly ahead of that shown by a neutral oxide. The neutralization of acidity with lime is less successful when accelerators that are very sensitive to acid conditions (butyraldehyde aniline) are used.

There are two testing problems before rubber technologists interested in zinc oxide: one is the choice of an oxide to fill specific needs and the understanding of its properties;

the other is testing to determine the uniformity of successive shipments. For the first purpose it is desirable to use rubber tests rather than to attempt to choose an oxide on the basis of chemical and physical specifications. For the determination of uniformity, pigment tests can be used, and the purpose of Part I of this paper (2) was to report pigment properties. Pigment tests, such as by analysis, screen, and microscope, may be desirable as short cuts to rubber tests, and the latter can be reserved for cases where pigment differences are noted.

In the rubber testing of zinc oxides, it is desirable to use (1) commercial formulas and (2) specific formulas that will bring out certain factors. For instance, in determining reinforcement, it is desirable to use a formula in which variations in rate of cure have been reduced to a minimum. For example, it would be well to choose an accelerator such as mercaptobenzothiazole that would be little affected by acidity. It would be desirable to use relatively high sulfur contents to eliminate the possibility of variations in cure due to adsorption of sulfur on the zinc oxide surface, and the addition of considerable quantities of fatty acid would tend to reduce variability in the rubber. A reasonably large amount of accelerator would also be a step in the right direction.

On the other hand, in testing for rate of cure, differences can be brought out best by using higher sulfur than is generally used in commercial practice, and relatively low accelerator contents. Since the rate of cure depends on the accelerator choice, several accelerators should be tried.

For activation, commercial formulas containing only 5 to 10 per cent of zinc oxide are satisfactory.

Color in rubber will depend on the acidity of the stock, and it is well to make tests in an alkaline mix such as may be used in footwear in order to obtain comparisons under severe conditions.

No series of tests is complete that does not include service requirements and factory-processing tests in addition to performance tests. Satisfactory tensile, flexing, and abrasion tests are no assurance that difficulties from design factors, such as foxings pulling from tennis shoe uppers and treads separating from tire carcasses, will not develop. The performance and service tests depend so greatly on special conditions that they must be considered as individual problems and therefore will not be discussed further here.

Suggested formulas for investigation are as follows:

	REINFORCING	RATE OF CURE	ACTIVATION	COLOR ALKALINE STOCK
Rubber	100	100	100	100
Sulfur	5	10	3	4
Mercaptobenzothiazole	2
Stearic acid	4	1	2	...
Zinc oxide	152 ^a	152	5-10	91 ^b
Accelerator	...	1/2-1/4	1/2-1	...
Thiocarbamide	2 1/2
Whiting	29 ^c
Hydrated lime	9 ^d

^a 25 volumes to 100 of rubber.

^b 15 volumes to 100 of rubber.

^c 10 volumes to 100 of rubber.

^d 4 volumes to 100 of rubber.

In the laboratory evaluation of zinc oxide, one runs into the well-known difficulties in connection with the variability of rubber testing. Tensile strengths are reported as force per unit of area, expressed in pounds per square inch or kilograms per square centimeter, which indicates that the test is absolute. Practically, however, it is found that even with controlled temperature and humidity during testing, the values change in unexplained ways from time to time, and it is desirable always to compare the oxide in question with a standard oxide; this involves the preparation of a considerable amount of uniform material which is more difficult than for coarse materials such as ore and coal. A practical method consists in spreading the oxide that is to be made uniform in a box, layer upon layer. When the oxide is all in place, one side of the box is removed, and the oxide is cut down in thin vertical layers and spread out again in horizontal layers in a second box below the first. This process is repeated a third time, and then the oxide is passed through a screen (approximately 40 to 60 mesh) to break up the groups. In this action the cylindrical bolter type of screen is chosen since the oxide receives additional mixing during screening. This uniform oxide should then be stored in a dry place and used as a standard of comparison. Where large numbers of tests are being run it will be desirable to have a control sample in addition to the standard, in order to extend the life of the standard and to compare the unknowns with the control sample, the standard being used only when a new lot of control oxide is chosen.

In the sampling of pigments for test, a "thief," consisting of a half-inch (1.27-cm.) brass pipe opened down one side for one-third of the circumference, can be inserted in a bag of oxide, and a representative sample withdrawn. After this sample has been passed through an ordinary kitchen flour sieve two or three times, it can safely be subdivided further for the various tests that are to be made. Taking up the various pigment tests, it will be found that there will be little need for chemical tests other than acidity, water-soluble salts, lead, cadmium, and grit.

SUGGESTED PROCEDURES

ACIDITY DETERMINATION. Place 5 grams of zinc oxide in 100 cc. of water at room temperature and shake by hand every 2 minutes for a period of 30 minutes. Add phenolphthalein and rapidly titrate the suspension of zinc oxide in cold water (room temperature) with 0.02 *N* sodium hydroxide until the pink color persists for a few moments. This test measures that part of the acidity that is effective in retarding cure. If the oxide is heated with an excess of alkali and then titrated back with acid, a value in line with the total sulfur is obtained.

WATER-SOLUBLE SALTS. Place 5 grams zinc oxide in 250 cc. water at room temperature and shake every 2 minutes

for 20 minutes. Filter and with the wash waters make up to 500 cc. Evaporate an aliquot portion of 200 cc. to dryness at 120° C. and weigh.

MATERIAL INSOLUBLE IN HYDROCHLORIC ACID. Moisten 5 grams zinc oxide with water in a 250-cc. beaker, add 25 cc. concentrated hydrochloric acid, evaporate to dryness; take up residue with 10 cc. concentrated hydrochloric acid, dilute to 125 cc. with distilled water, boil and filter residue, and wash residue several times with hot dilute hydrochloric acid and finally three to four times with hot water. Ignite in a weighed porcelain crucible.

LEAD. Weigh 10–100 grams oxide (depending on whether lead is expected to be 0.5–0.01 per cent) into a 600-cc. beaker,

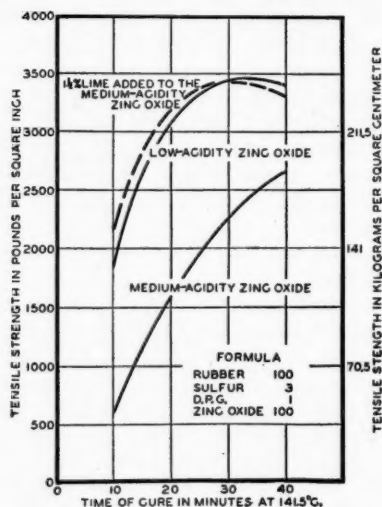
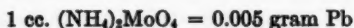


FIGURE 1. EFFECT OF HYDRATED LIME IN NEUTRALIZING ACIDITY OF ZINC OXIDE CARRYING 0.2 PER CENT ACIDITY

and add 400 cc. distilled water and 50 cc. concentrated sulfuric acid. Boil till zinc oxide is dissolved. Cool with ice, filter, and wash two or three times with cold distilled water. Place the filter paper containing precipitate back into original beaker, add 30 cc. of ammonium acetate and 50 cc. of hot water, and boil to dissolve lead sulfate. Dilute to 300 cc. with hot water and titrate at once with ammonium molybdate (4.34 grams per liter), using tannic acid as an indicator:



The electrolytic method by which lead is deposited on the anode from a nitric acid solution is preferred by some laboratories.

CADMIUM. Treat 5 grams zinc oxide in a 250-cc. beaker with 10 cc. concentrated hydrochloric acid, evaporate to dryness, add 10 cc. concentrated sulfuric acid, and heat to sulfur trioxide fumes. Cool and add 125 cc. water. Wash residue several times with water and bring filtrate to 200 cc. Heat filtrate to boiling and saturate with hydrogen sulfide, cooling toward the end to insure complete precipitation of cadmium sulfide. Filter, wash, dissolve precipitate with 25 cc. of 1:2 hydrochloric acid, and wash with hot water. Evaporate filtrate almost to dryness, add 10 cc. concentrated sulfuric acid, and heat to sulfur trioxide fumes. Cool, add 125 cc. water, boil, cool, filter, and wash residue several times with water till filtrate comes to 200 cc. Heat filtrate to boiling and saturate with hydrogen sulfide as before. Three precipitations remove the zinc completely. After the third precipitation, filter off cadmium sulfide in a weighed Gooch crucible, wash with water, dry at 115° C., and weigh as cadmium sulfide.

FATTY ACID. Whether or not zinc oxide has been surface-treated with fatty acid can be determined qualitatively by adding it to water in a beaker. Zinc oxide treated with fatty acid is poorly wet and will float on the surface of the clear water, whereas untreated oxide will sink and make an opaque suspension.

To make the determination quantitative, 10 grams of zinc oxide can be wetted with a little alcohol and taken up with water. The zinc oxide can be dissolved with dilute sulfuric acid making a volume of about 200 cc. The solution is transferred to a 500-cc. separatory funnel, using ether to wash out the beaker. After three extractions with 50 cc. of ether, the ethereal solution is evaporated in a tared evaporating dish, and the fatty acid is recovered and weighed or titrated. It may be dark colored owing to its having been added while the oxide was at so high a temperature that some decomposition occurred.

PARTICLE SIZE. In the case of coarse pigments, direct microscopic observation can be made and the particle size can be determined either by comparison with a standard slide or by photographing and measuring on a screen (4). Rubber pigments frequently contain a large percentage of particles below the resolving power of the microscope, and this method can be used only on the coarser particles. In order to study the fine material, the number of particles in a unit volume of a pigment suspension are counted by use of the microscope, using dark-ground illumination and well-established colloid methods. Dispersion in rubber followed by diluting with solvents has been shown to be desirable by Gehman and Morris (5). These authors have also discussed the use of opacity tests, which undoubtedly have considerable value for control work. They show that the opacity depends upon the color of the light, and other investi-

gators have found that, by examining the difference between the red and blue opacity values, an indication of the uniformity of particle size can be obtained.

It would be ideal to separate pigments into size ranges and to learn the percentages present of each size as is done by screen analyses in the case of coarser materials. Since the openings in screens are too large to be significant, this method cannot be used, but a method has been described by Seguire (5) based on centrifuging a suspension and measuring the rate of settling, which offers hope as a future tool. Centrifuging into fractions and determining the amount and average particle size of each fraction is another possible method of attack. Here optical equipment might be used with advantage.

To define properly the physical characteristics of a zinc oxide, it would be desirable to report four properties of which the first three would be most important:

1. Average size (dark-ground count)
2. Uniformity of size [slope of the size-distribution curve as in Figure 3 (2)]
3. Average shape (deviate from sphericity)
4. Uniformity of shape

PARTICLE SHAPE. In the case of coarser particles, the particle shape can be determined by direct observation under the microscope, as with particle size. But in the case of the finer particles, this is impossible. An indication can be obtained, however, by dispersing the pigment in a good wetting medium and observing it under dark-ground illumination. The particles which will be in Brownian movement will twinkle if irregular in shape. As an alternative, the Szegvari Azimuth Stop will illuminate the microscopic field from changing angles and help determine whether the particles are needles or otherwise.

If the average amount of surface per particle could be determined, it should be possible to find the departure from sphericity (i. e., acicular tendency in the case of zinc oxide) by obtaining the ratio of surface to diameter.

For determining the amount of surface, the Bartell-Osterhof cell (1) has been suggested, and methods of adsorbing a molecular layer from a gas may also be worked out. Work and Odel (6) have suggested the adsorption of water vapor in the case of lithopone, but nonhygroscopic vapors would have to be used for zinc oxide since hygroscopic zinc sulfate would interfere.

GRIT. The most general method of determining grit is to place 100 grams of zinc oxide on a 100-mesh screen and wash it through with a stream of water, applying gentle brushing with a half-inch (1.27-cm.) paint brush. The screen carrying the residue is dried in an oven, and the dry residue is brushed on to a balance pan and weighed. The weight, however, is of less importance than the character

of the dirt, a hard sharp material being considered more objectionable than soft material. It takes considerable experience and judgment to evaluate properly the quality of the small amounts of grit found.

WHITENING STRENGTH AND COLOR. The color of the pigment can be determined by rubbing it down with pale bleached linseed oil and comparing with a standard. An approximate value can also be obtained by placing the test material beside a standard in piles, pressing a watch glass down over the piles, and comparing them at the boundary line.

The whitening-strength test, which is more significant, can be made by rubbing down 2 grams of pigment with 20 milligrams of ultramarine blue and 20 drops of pale bleached linseed oil, and comparing with a standard; the oxide that develops the paler blue has the higher whitening strength. The test can be made quantitative by varying the amount of blue until the standard and unknown develop the same tint, the relative whitening strengths being directly proportional to the amount of blue required.

It might be assumed from this discussion that zinc oxide furnished by the manufacturers is far from uniform. As a matter of fact, the uniformity is very high and most technologists have found that control tests are generally unnecessary. When a check is desired, however, the methods that have been discussed should be helpful.

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CORRECTION

The Problem of Changes in Rubber Brought about by Atmospheric Oxygen

Charles Dufraisse

This article published in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. VI, No. 2 pages 157-192, April, 1933, contained a bibliography of two hundred forty-four references to original articles.

In seven cases the original articles actually are as follows:

Reference number	Original source
15	<i>Chem.-Ztg.</i> , 31, 638 (1907)
47	<i>India Rubber J.</i> , 61, 1163 (1921)
79	<i>Kautschuk</i> , 2, 57 (1926)
161	Gottlob, <i>Technologie der Kautschukwaren</i> , 1925, page 176
194	<i>Rev. gén. colloides</i> , 1, 33 (1923)
244	<i>Trans. Inst. Rubber Ind.</i> , 3, 151 (1927)

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